THERMAL DEGRADATION OF POLYESTERS

PART II. AROMATIC AND SEMIAROMATIC POLYMERS

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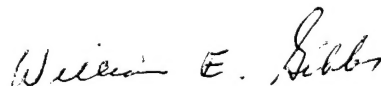
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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task 734203, "Fundamental Principals Determining the Behavior of Macromolecules." It was administered under the direction of the Air Force Materials Laboratory with Dr. I. J. Goldfarb (MANP) as Task Scientist.

This report covers work conducted from 1 July 1967 to 1 July 1968.

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This technical report has been reviewed and is approved.

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ABSTRACT

A detailed study was made of the thermal degradation of eight aliphatic polyesters and the results presented in Part I of this report. The results of a corresponding study of some polyesters containing aromatic rings in the polymer chain are now presented in Part II.

Poly(hexamethylene terephthalate) degrades by the mechanism observed for aliphatic polymers -- random scission and subsequent reaction of the olefinic and acid end-groups. When the acid part is aliphatic as in poly(1,4-phenylene succinate) and poly(1,4-phenylene sebacate), the polymers are less stable initially than comparable aliphatic polyesters. The degradation mechanism is more complex and involves cross-linking; the cross-linked sebacate product breaks down by a second degradation reaction but the succinate forms a residue which does not undergo further breakdown.

Fully aromatic systems studied, namely poly(1,4-phenylene terephthalate), poly(1,3-phenylene isophthalate), poly(1,4-phenylene isophthalate-co-terephthalate) and poly(4,4'-biphenylene isophthalate), were more thermally stable, especially the all para system, and 35 to 45% of the initial weight remained at 800°C. Features such as initial low activation energy processes, complex rate curves with several components and char formation at high temperatures imposed difficulties in kinetic analysis of the degradations by programmed thermogravimetry.

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INTRODUCTION

The purpose of this study has been to investigate the effect of structure on the thermal degradation mechanisms of polyesters. The kinetics, products, and mechanisms of degradation of aliphatic polymers have been previously presented (Reference 1); it was found that degradation could be best explained in terms of decomposition of the ester linkage by the classical concerted reaction observed for the pyrolysis of simple esters. The newly formed end-groups decomposed by secondary reactions and, depending upon the structure of the end-groups, decarboxylation, anhydride formation, and cyclic ketone formation from acid ends and diene, cyclic ether, unsaturated alcohol, and aldehyde formation from unsaturated end-groups were observed. An overall random mechanism with activation energies in the range 35 to 41 kcal-mole^{-1} was concluded.

In this report, the investigation is extended to polyesters containing aromatic structures in the chain. To bridge the gap between aliphatic systems and fully aromatic polymers, three "semiaromatic" polyesters were examined; in the preparation of these polymers, polycondensation of a diol and a diacid, one of the reactants was aliphatic and the other aromatic. Poly(1, 4-phenylene succinate) and poly(1,4-phenylene sebacate) can be compared to the aliphatic succinate and sebacates of the previous study. Poly(hexamethylene terephthalate) provides the contrasting case of the aromatic ring located in the acid moiety. The thermal characteristics of this polymer can be compared with poly(ethylene terephthalate), which has been the subject of many investigations (References 2 and 3, for example).

Four fully aromatic polymers were also studied: poly(1, 4-phenylene terephthalate), poly(1, 3-phenylene isophthalate), poly(1, 4-phenylene isophthalate-co-terephthalate) and poly(4, 4'-biphenylene isophthalate). Using these polymers, the influence of the aromatic ring on the thermal stability can be further evaluated and the effect of different aromatic structures examined.

Rates of weight loss were measured by temperature programmed thermogravimetry and kinetic analysis attempted. Additional information was obtained by mass spectrometric thermal analysis. Volatile degradation products were examined by mass spectrometry, and residues and nonvolatile products by infrared spectroscopy.

SECTION II

REVIEW

Because of its commercial importance, the semiaromatic poly(ethylene terephthalate) has been the subject of numerous degradation studies (References 2 through 5). Since the alkyl part of the ester has a hydrogen atom beta to the ester group, the first step in the degradation is the classical ester scission (Reference 6), giving carboxylic acid and olefinic end-groups. Secondary breakdown of the vinyl phthalate groups gives acetaldehyde as the major volatile product. Decarboxylation of the acid end-groups is the other important reaction producing volatile products. Various values of activation energy depending on the method of determination are reported in Reference 3; the value of about 45 kcal-mole^{-1} found by acid group titration is in good agreement with that observed for the decomposition of model compounds. Marshall and Todd give a lower value of 32 kcal-mole^{-1} based on viscosity measurements.

Comparing poly(ethylene terephthalate) with aliphatic polyesters, there is no increase in thermal stability for the semiaromatic polymer. This agrees with the observation that simple benzoate esters degrade at comparable if not higher rates than simple aliphatic esters under the same conditions (Reference 7); this was explained in terms of increased nucleophilicity of the carbonyl oxygen atom adjacent to the aromatic ring.

Several aromatic polyesters have been studied in Reference 8, one of which was the mixed isophthalate-terephthalate being examined in the present study. At temperatures up to 450°C, carbon monoxide and carbon dioxide are the major volatile products, but a considerable amount of sublimate (hydroquinone) is also formed. At higher temperatures, formation of the sublimate fraction ceases and carbon monoxide and hydrogen increase in importance relative to the carbon dioxide. The authors concluded that some ring fragmentation occurs in the temperature range 460° to 520°C but the main reaction appears to be the rupture of ester linkages with reformation of radicals to cross-linked polyphenyl and polyphenylether structures. Another polymer studied in Reference 8 is that derived from isophthalic acid and bisphenol A. This is similar to the biphenylene polymer being studied here but has isopropylidene groups separating the two rings of the biphenylene moiety. The aliphatic group results in higher yields of hydrogen and methane, but below 450°C carbon monoxide and dioxide are again the major volatile products. The sublimate outweighs the volatile fraction by about four to one. At higher temperatures, the relative importance of the carbon dioxide diminishes and hydrogen becomes the major product in mole percent terms.

SECTION III

EXPERIMENTAL

1. POLYMERS

Polyhexamethylene terephthalate was prepared from hexamethylene glycol and terephthalyl chloride by the anhydrous melt reaction described in Reference 9(a). The polymer was dissolved in hot DMF and precipitated in methanol. The white fibrous polymer was then dried overnight in a vacuum oven at 80°C.

Poly(1,4-phenylene succinate) and poly(1,4-phenylene sebacate) were prepared by the method described in Reference 9(b); this consists of the acidolysis reaction between p-phenylene diacetate and the free dibasic acid. The products were ground to a powder and stored for several days at 100°C in a vacuum oven. (Reprecipitation was not done when solubility was limited to high boiling solvents such as m-cresol).

Poly(1,4-phenylene terephthalate) was prepared from hydroquinone (sodium salt) and terephthalyl chloride by the interfacial technique (Reference 10). The polymer was washed several times with hot water, Soxhlet extracted with acetone and dried in vacuo at 100°C.

Poly(4,4'-biphenylene isophthalate) and poly(1,3-phenylene isophthalate) were prepared interfacially by Dr. R. C. Evers of the Polymer Branch, Air Force Materials Laboratory (AFML), to whom we are grateful for samples of the polymers.
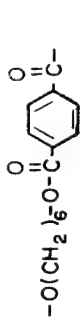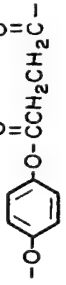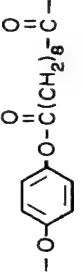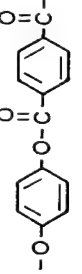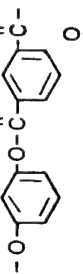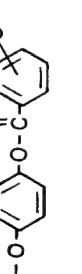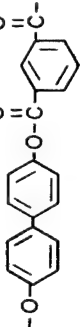
Poly(1,4-phenylene isophthalate-co-terephthalate) was obtained from the General Electric Company by Dr. G. F. L. Ehlers of the AFML. This experimental polymer (GE-K28R) was prepared from hydroquinone and an 85 to 15% mixture of isophthaloyl and terephthalyl chlorides in chlorinated diphenyl ether at 300°C.

The above polymers and some relevant properties are listed in Table I.

Preliminary evaluation of the polymers by thermogravimetry was done prior to detailed kinetic analysis. It was generally found that those polymers which had been subjected to high temperatures during polycondensation and those which were soluble enough to be purified by reprecipitation gave no weight loss before the main degradation started. Polymers which did not fulfill these requirements, i.e., PS, PT and BP (symbols defined in Table I), had very

TABLE I

LIST OF POLYMERS STUDIED

Polymer Name Poly –	Symbol	Repeat Unit	Melting Point (or softening) (°C)	Elemental Analysis				Other Properties
				Theoretical(%)		Found(%)		
				C	H	C	H	
hexamethylene terephthalate	HT	[structure: $-O(CH_2)_6-O-C(=O)-\text{phenyl}-C(=O)-$]	150	67.75	6.50	68.51	6.82	Soluble in hot DMF, m-cresol
1,4-phenylene succinate	PS	[structure: $-O-\text{phenyl}-O-CCH_2CH_2C-$ (with =O groups)]	314	62.50	4.20	61.10	4.22	Soluble in 40/60 sym-tetrachloro-ethane, phenol
1,4-phenylene sebacate	SP	[structure: $-O-\text{phenyl}-O-C(CH_2)_8-C-$ (with =O groups)]	176	69.55	7.30	68.34	8.22	Soluble in m-cresol and solvent for PS
1,4-phenylene terephthalate	PT	[structure: $-O-\text{phenyl}-O-C(=O)-\text{phenyl}-C(=O)-$]	>400	70.00	3.36	69.18	3.40	
1,3-phenylene isophthalate	PI	[structure: meta-phenylene diester]	290	70.00	3.36	69.70	3.35	Soluble in m-cresol $\eta_{inh}=0.29$ $T_g = 209°C$
1,4-phenylene iso-phthalate-co-terephthalate	PP	[structure: copolymer iso/tereph diester]	385	70.00	3.36	69.90	3.35	Soluble in 2,4,6 trichlorophenol $[\eta] = 1.04*$ $T_g = 300*°C$
4,4'-biphenylene isophthalate	BP	[structure: $-O-\text{biphenyl}-O-C(=O)-\text{phenyl}-C(=O)-$]	>360	75.94	3.82	74.50	3.80	$T_g = 310°C$

* Reference 8

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noticeable weight losses starting at low temperatures. Since early "bleeding" could create errors in the intended analysis, it was desirable to eliminate such weight losses. This was done by heating the polymers isothermally at temperatures which would allow the low temperature reaction to take place but not true degradation. PS was heated in vacuo for two hours at 250°C, PT and BP for two hours at 300° to 350°C; the polymers did not melt during the heat treatment. The treated polymers showed considerably improved weight loss curves as illustrated in Figure 1. The materials distilling out were examined by IR spectroscopy and found to be hydroquinone for PS, terephthalic acid and a little low molecular weight (MW) polyester for PT and the biphenol plus a little low MW polymer for BP. Thus, the preheating process appeared to remove low MW material from the polymer although interchange reactions could also explain the formation of some products. Elemental analyses of the heated polymers were closer to the theoretical figures than those of the original materials.

2. THERMOGRAVIMETRIC ANALYSIS (TGA)

The apparatus and procedure used have been described in detail as has the method of kinetic analysis (References 1, 11 and 12). A brief summary of the procedure is given below.

Using an "Ainsworth" thermobalance, 50 to 100 mg samples were degraded under high vacuum conditions. Heating rates were in the range 75° to 450°/hr and each polymer was studied at a minimum of four heating rates. Since most of the polymers melt or at least soften prior to or during degradation, the initial partial size was not rigorously controlled.

From the primary weight-temperature charts, rates of weight loss and temperatures were computed for unit increments in sample weight loss; where the reaction under investigation could be assigned a weight loss less than the sample weight, as in cases involving residue formation or two separate degradation reactions, this partial weight loss was used as the basis for rates and conversion computations. For each conversion, a series of rates and temperatures are obtained for the varying heating rates employed and the activation energy for each conversion is obtained from plots of log rate against reciprocal temperature in accord with Equation 1.

$$\log \frac{1}{W'} \cdot \frac{dW}{dt_B} = \log A + \log F(W) - \frac{E_a}{2 \cdot 3R} \cdot \frac{1}{T_B} \qquad (1)$$

In this equation, W' is weight available for the reaction being studied, e.g., for a curve showing a single step and a residual weight (W_f), $W' = W_o - W_f$; $F(W)$ is an unknown function of

function of weight assumed to be constant at fixed weight loss increments (W/W'). The suffix B indicates the dependence of rate and temperature on heating rate. The other symbols have their usual connotations.

For simple cases, an average value of E_a can be calculated and Equation 1 rearranged to compute log A F(W) (= log A + log F(W)), which is plotted against log (percent remaining), i.e., log (1-W/W'). The shape of the resulting curve or line gives information about the functionality term, F(W), and the rate law governing the kinetics. If F(W) can be evaluated, the preexponential factor, A, can be calculated, thus completing the analysis.

Calculations were done using an IBM 7094 computer. Details of the computer programming are given in Reference 12.

3. ANALYTICAL METHODS

a. Mass Spectrometric Thermal Analysis (MTA)

Polymer samples were submitted for MTA to Dr. H. Friedman of the General Electric Company under USAF contract. The apparatus and technique are described in References 13 and 14. The use of MTA data in the present research is discussed in Reference 1.

b. Mass Spectrometry (MS)

Supplementary product analysis was performed for volatile fractions obtained from closed system isothermal degradation. The analyses were done by Mr. W. R. Powell of the Analytical Branch, AFML, using a Consolidated Electrodynamics Corporation Model 21-103B mass spectrometer at an ionizing voltage of 70 V and current of 10μ amp.

c. Infrared Spectroscopy

A Perkin-Elmer Model 137 spectrophotometer was used; solids were examined as pressed KBr films, liquids as films between salt plates.

d. Elemental Analysis

Analyses were done in duplicate by the AFML Analytical Branch. Data represents mean values.

SECTION IV

RESULTS AND DISCUSSION

1. TGA STUDIES AND KINETIC ANALYSIS

Representative weight loss curves are given in Figure 2. The semiaromatic polymers degrade at lower temperatures than the aromatic polymers; only HT showed complete sample weight loss, SP giving about 2% residue and PS about 12% residue at 600°C. The aromatic polymers gave higher residual weights, 35 to 45% sample weight (SW) at 700°C. These polymers, and also PS, could not be assigned an ultimate residue weight since the samples were still losing weight very slowly at 800°C, the limit used with the apparatus. Thus, a slow reaction is taking place at high temperatures in these polymers, giving a long "tail" in the TGA curves.

When the derivative rate (DTG) curves are examined (Figures 3 and 4), other features become obvious. In these Figures, rates have been calculated on a percent SW basis, which is satisfactory for qualitative comparisons. Most of the polymers exhibit a single rate maximum; SP, however, shows two maxima and BP has a distinct shoulder on the high temperature side of its curve. In addition to high temperature tails previously mentioned, it appears that some polymers, notably SP and PT, have tails on the low temperature side also. In Figure 3, two aliphatic polyesters from Reference 1 were included for comparison; the semiaromatic polymers are less stable with respect to initial rates than comparable aliphatic systems. It is surprising that PS is less stable than any of the aliphatic polymers previously studied. HT also is relatively unstable being similar to the least stable aliphatic polymer studied (01). HT is characterized by an extremely sharp curve and high rate maximum.

Figures 5 and 6 show the corresponding rate-weight loss curves. HT gives a simple curve similar to those observed for aliphatic polymers. The irregularities in behavior of the other polymers are again evident. These curves are useful for attempting to deduce fractional weights corresponding to a single component of the degradation and will be referred to again in subsequent stages of the analyses.

Activation energy trends are shown in Figures 7 and 8. For these illustrations, 100% conversion is arbitrarily defined for each polymer as a suitable weight loss range within which meaningful values of E_a could be calculated. Preliminary computations on a percent sample weight-loss basis showed that calculations in the "tail" region of the curves were

subject to large errors, unit increases in weight loss requiring large temperature increases. The conversion range was therefore redefined to cut off most of the tail region. This truncation does not resolve anything but gives an expanded picture of the overall weight loss range. Most of the polymers show regions where the activation energy is reasonably constant. SP clearly shows the E_a levels corresponding to the two components in the rate curves; where the two reactions overlap the apparent E_a gradually increases from the lower value to the higher value. The initial high values of E_a observed for PS are probably erroneous since the inclusion of superimposed initial reactions in the calculation is a potential source of error. Polymers PP and BP are somewhat abnormal since the activation energy is approximately constant for only a limited region at lower conversions after which E_a increases almost continuously.

For the relatively simple case of HT, the analysis is easily extended to investigate the weight function term (Equation 1). The term "conversion" is unequivocal since complete weight loss occurs by a single kinetic scheme. The log A F(W) plot (see Section III. 2) is shown in Figure 9. The curve has a maximum value at 20 to 25% conversion and tends to unit slope at high conversions. This is the same behavior as that observed for aliphatic polymers and an overall random mechanism can be concluded. Since,

$$\log \left[A\ F(W) \right] = \log A + \log L/e + 2.0 \ (\text{Reference 1})$$

and L = smallest chain length which does not distill under degradation
conditions

$$\cong 4$$

an approximate value of A can be calculated (Table II).

Polymer SP has two components which can be approximately resolved by dividing the overall DTG curves into two individual overlapping curves. A useful guide in the resolution is that each component curve should be similar to the HT curve in Figure 5 and exhibit a rate maximum at 55 to 60% conversion of the component. This argument is based on theoretical rate-conversion curves (Reference 15) which show that the two common mechanisms, namely random and pseudo-first order, have rate maximums in this conversion range.

The total weight loss of SP was divided into components I and II in the ratio 73:27. Rates and temperatures were recalculated as a function of component conversion and individual log A F(W) plots constructed. These are shown in Figure 10 in which the overall plot obtained by treating the weight loss as one reaction is included for comparison. A random mechanism

was concluded for the first reaction although a superimposed initial reaction masks the maximum at 25% conversion. The second component could be random also but since the initial stages of component II depend on the hand-drawn resolution, no definite conclusion can be made; the slope at higher conversions is compatible with both random and first-order mechanisms.

When the end of the main degradation reaction is masked by the tailing process, the log A F(W) plot is distorted in the unresolved region since the average E_a assumed in the computation is that for the main degradation and not that for the complexing reaction. This is illustrated by the plot for PS (Figure 11) in which the random curve changes slope at high conversions. The corresponding curve of PT also given in this Figure is further complicated by the presence of an initial tail component in addition to the high temperature tail component. The incorporation of components other than the one for which analysis is being attempted has another consequence; the true conversion of the component is less than that assumed in the plot so that the true curve is compacted into a smaller conversion range producing higher slopes than should be obtained. It is critically important, therefore, to realize that if the correct conversion has not been used in the plot, apparent orders (slopes) may be drastically wrong. Slopes as high as 5 can be observed at high conversions instead of near unity for the pure component.

The above considerations are again evidenced in the curves for the remaining polymers (Figure 12), and a discussion of the curves for PI would parallel that for PT. The results for PP were computed at first on the basis that 65% sample weight loss constituted 100% conversion; the apparent slope at high conversions in the log A F(W) plot approached 5.0. Recalculation of the data for 50% SW = 100% conversion reduced the slope to 1.6. The overall curve shown for BP is very complex. The initial reaction does not mask the maximum of the random degradation component. A change of slope shows the second component and there is probably a "tail effect" at even higher conversions. Because of the degree of overlap of the two major components in BP, the resolution previously done for the SP case was not attempted in this instance. The information obtained from these analyses is summarized in Table II.

2. PRODUCTS OF DEGRADATION

Products which distilled out of the hot degradation zone were subdivided into condensates which condensed on cooler parts of the degradation column immediately above the furnace, and a more volatile fraction, part of which condensed in a liquid nitrogen trap. The two

TABLE II

KINETIC PARAMETERS

Polymer	Type of Process	SW Loss % *	Average E_a (kcal-mole^{-1})	Average Deviation ** (kcal-mole^{-1})	Average Characteristics	Kinetic Type	Approximate A from log A F(W) Data (min^{-1})
HT	ester degradation	0-100	47.1	2.0	maximum at 24% conversion	random	1.2 x 10^{15}
PS	ester degradation	0-65	46.0	4.0	maximum type	random	1.5 x 10^{16}
	char forming tail	65-90	—	—	—	—	—
SP	component I	0-40	31.0	2.5	maximum type with overlapping initial process	random	7.6 x 10^{8}
	(intermediate)	40-80	31.0 57.5	—	—	—	—
	component II	80-98	57.5	1.5	uncertain	random or first order	3.2 x 10^{16}
PI	Initial "bleed"	0-20	36	—	—	—	—
	ester degradation	20-65	48.1	1.0	maximum masked by initial process	probably random	2.5 x 10^{13}
	char formation	65→	—	—	—	—	—
PT	Initial "bleed"	0-20	—	—	—	—	—
	ester degradation	20-60	76.0	2.5	maximum masked by initial process	probably random	1.5 x 10^{19}
	char formation	60→	—	—	—	—	—

TABLE II (Contd)

Polymer	Type of Process	SW Loss* %	Average E_a (kcal-mole^{-1})	Average Deviation** (kcal-mole^{-1})	Average Characteristics	Kinetic Type	Approximate A from log A F(W) Data (min^{-1})
PP	Initial "bleed"	0 - 20	—	—	—	—	—
	ester degradation	5 - 25	62.0	4.0	maximum type	random	1.9×10^{16}
	changing degradation	25 →	76,90	—	—	—	—
BP	Initial "bleed"	0 - 3	—	—	—	—	—
	component I	3 - 26	52.0	2.0	maximum type	random	4.0×10^{14}
	component II	26 - 40	65.0	5.0	—	—	$\sim 10^{18}$
	char formation	40 →	—	—	—	—	—

* Because of overlap in multicomponent degradation, the weight loss ranges are approximate.

** Average least square deviation for slopes of individual E_a plots.

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fractions are arbitrarily termed condensates and volatiles in the following discussion. As has been previously noted, residues were also formed for many of the polymers and merit a brief discussion.

a. Residues

The residues retrieved after programmed degradation to around $700°C$ were examined. The black flaky appearance of the residues from PS, PI, and PP suggested that melting or softening had taken place during or prior to degradation but the residues from PT and BP were finely divided, black powders which did not appear to have softened. Elemental analysis showed that the residues were highly carbonized (Table III). Since the analysis figures did not add up to 100% (probably because of incomplete combustion), it is difficult to obtain any structural information from the results. To gain some insight into the residue formation, some isothermal studies were carried out to yield partially formed residues; these degradations are summarized in Table IV. The residues were compared with the starting materials by IR spectroscopy (see Figures 13 through 19). In general, the spectra of the residues are similar to those of the original polymers, but some small changes are apparent.

Polymer HT shows a new band at 1780 cm^{-1} region probably results from acid groups. The succinate part of the PS polymer appears to have changed although the ester absorptions remain intense. The fully aromatic polymers also exhibit new carbonyl absorptions but these occur in the lower 1650 to 1675 cm^{-1} range; diaryl ketone formation would explain these new peaks. In all cases, the ester bands remained strong. Reduced intensities in the finger print region and changes in the substitution patterns of some of the polymers may be indications of cross-linking.

b. Condensates

It has been shown in Table IV that the condensate fraction constitutes most of the total weight loss. In most cases, the condensate was observed to consist of a series of layers suggesting several types of products. Because of the considerable overlapping, weight analysis of the components was not attempted. Information deduced from the IR spectra (Figures 13 through 19) is summarized in Tables V and VI. These observations apply to the condensates from both programmed and isothermal studies. In many instances, pure components were identified but the lower waxes were probably mixtures of several oligomeric species. The arylene polymers give significant amounts of the phenol used to make the polymer but not the diacid. Some acid group formation is observed, but normally decarboxylation occurs before

TABLE III

ELEMENTAL ANALYSIS OF TGA RESIDUES

Polymer (°C)	$W_{Residue}$ (% SW)	ANALYSIS		
		C (%)	H (%)	O (%)
PS 600-650)	12	88.8	2.1	4.0
PI 700	33	90.5	2.7	3.5
PT 700	35	92.0	2.5	2.9
PP 700	35	92.5	2.7	3.0
BP 700	42	91.4	2.6	2.5

TABLE IV

ISOTHERMAL DEGRADATIONS

Polymer	Time Temperature (of Degradation)		$W_{Residue}$	$W_{Condensate}$	$W_{Volatiles}$
	(hr)	(°C)	as % SW		(by difference)
HT	2.25	345	14.0	82.3	3.7
SP	2.0	350	45.5	50.3	4.2
PS	2.0	325	38.6	54.7	6.7
PI	2.0	420	57.0	41.5	1.5
PT	3.0	500	60.0	25.1	14.9
PP	2.0	450	82.4	15.5	2.1
BP	2.0	470	65.5	23.8	10.7

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TABLE V

CONDENSATES FROM DEGRADATION OF SEMIAROMATIC POLYESTERS

Polymer	Appearance of Condensate	Structure(s)
HT	single condensate: white wax	low MW polyester with acid end groups and possibly some C = C end groups
PS	lower: white crystals	hydroxy ester of type: HO—⬡—C(=O)—CH$_2$CH$_2$—CO—⬡—OH
	upper: brown wax + yellow crystals	hydroquinone with a little succinic anhydride
SP	1 (nearest hot zone) yellow wax	polyester
	2 yellow wax	low MW polyester with acid and hydroxyl end groups
	3 white crystals	hydroquinone: HO—⬡—OH
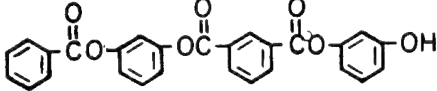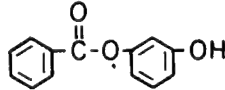
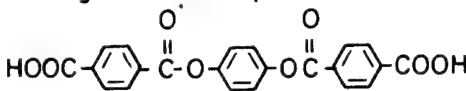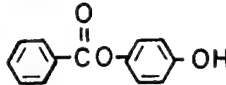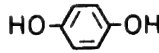the second acid group is formed by scission of the adjacent ester group. It is also evident from the considerable number of phenolic structures that many of the ester scissions are of the acyl-oxy type giving carbonyl radicals rather than carboxyl radicals. The intermediate carbonyl radical could recombine with other radicals or decarbonylate to form a benzoate end-group. Benzoate structures are observed in some of the hydroxyester type condensates, e.g., m-hydroxyphenyl benzoate from PI.

The terminal structures are all hydrogen rich so that the intermediate radicals formed by ester scission must abstract hydrogen from neighboring aromatic rings; in fully aromatic polymers, this is the only source of hydrogen. Residue formation is probably a consequence of recombination of the rings from which hydrogen has been abstracted.

c. Volatile Products

The volatile fractions obtained from isothermal experiments (Table IV) were collected in a liquid nitrogen trap and analyzed by mass spectrometry. Since the degradations were done in a closed system, the samples contained a known volume fraction of noncondensable

TABLE VI

CONDENSATES FROM DEGRADATION OF AROMATIC POLYMERS PI AND PT

Polymer	Appearance of Condensate		Structure(s)
PI	1 (nearest hot zone) clear wax		hydroxyester of type:
	2	white crystals	m- hydroxyphenyl benzoate:
	3	yellow oil	
	4	white powder	resorcinol:
	5	yellow crystals	probably mixture of resorcinol and benzoic acid
PT	1 (nearest furnace) white powder		polyester: small changes in IR caused by phenyl and benzoate end-groups
	2	brown powder	
	3	grey powder	
	4	green powder	ester with acid end-groups
	5	grey-green powder	strong acid absorptions:
	6	brown wax	hydroxyester:
	7	light brown material	
	8	yellow crystals	hydroquinone:

materials, e.g., CO, CH_4, H_2. The initial data was recalculated to correct the partial non-condensable contents and the results are given in Tables VIII and IX. Polymer HT gives considerable amounts of olefins and dienes derived from the C_6 aliphatic chain in the polymer. The product distribution follows the pattern previously observed for poly(ethylene terephthalate) and aliphatic polyesters. One important difference is observed when comparing the latter group to HT; aliphatic polymers give much higher yields of water. Polymer SP gives small amounts of hydrocarbons indicating some fragmentation of the sebacate part. In contrast, PS

TABLE VII

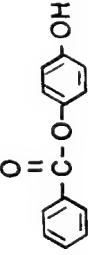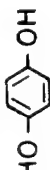### CONDENSATES FROM DEGRADATION OF AROMATIC POLYMER PP AND BP
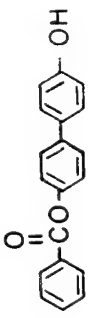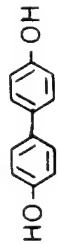
POLYMER	APPEARANCE OF CONDENSATE	STRUCTURE(S)
PP	Lower - yellow wax	low MW polyester and hydroxy-ester:
	upper - white crystal	hydroquinone:
BP	I (nearest furnace) light brown material	low MW polyester with some hydroxy ester and possibly some ketonic groups
	2 - yellow wax	hydroxyester:
	3 - yellow crystals	p, p' - biphenol:
	4 - white crystals	phenolic compound, probably:

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TABLE VIII

MASS SPECTROMETRIC ANALYSIS OF VOLATILES FROM
SEMIAROMATIC POLYMERS

PRODUCT	HT	PS (mole %)	SP
Carbon Dioxide	16.1	68.4	77.7
Carbon Monoxide	6.7	30.6	10.0
Water	1.2	0.4	0.4
Hydrogen	1.0	0.4	1.3
Methane	2.9	0.2	3.8
Ethene	5.7		
Propene	4.5		
1,5-Hexadiene	38.0		
Cyclohexene	18.6		
1,3-Cyclohexadiene	0.6		
1,4-Butadiene	1.8		
1-Butene	2.9		1.2
Butane			4.9
Cyclopentene			0.4
1-Pentene			1.2

gives no products corresponding to the succinate moiety (succinic anhydride is observed in the condensate fraction). For PS and all the aromatic polymers, carbon monoxide and carbon dioxide make up more than 95% of the volatile fraction with minor amounts of hydrogen, methane, water, benzene, and toluene.

Volatile products were also examined from MTA spectra; bar graphs derived from these are illustrated in Figures 20 and 21. The data of the semiaromatic polymers is consistent with the previous MS results. The HT spectrum is dominated by peaks derived from the aliphatic C_6 chain -- especially the cyclohexene and/or hexadiene product. As in the case of

TABLE IX
MASS SPECTROMETRIC ANALYSIS OF VOLATILES FROM
AROMATIC POLYMERS

PRODUCT	PI		PP (mole %)	PT	BP
	*	**			
Carbon Dioxide	78.1	67.1	34.3	49.1	77.3
Carbon Monoxide	20.2	29.2	63.3	49.6	17.4
Water	0.1	0.9	0.1	0.2	1.4
Hydrogen	†	0.3	†	†	0.9
Methane	0.7	0.7	2.0	0.1	0.5
Benzene	0.4	1.7	0.1	1.0	2.5
Toluene	0.5	0.1	0.2	–	–

* Isothermal degradation at 420 °C
** Isothermal degradation at 444 °C
† Hydrogen not analyzed because of instrumentation error

aliphatic polyesters, a very small peak corresponding to the olefin plus water is observed at $M/e = 100$. A major difference for HT was that the contributions of water and carbon dioxide were unusually small. The aromatic acid groups appear to be relatively stable to decarboxylation. The products for PS are carbon monoxide, carbon dioxide, succinic anhydride, and a little water. The anhydride gives the strong $M/e = 56$ fragment and makes a strong contribution to the $M/e = 28$ peak (40%); CO and CO_2 are again the major products for SP. A large number of trace products is evident, indicating fragmentation of the sebacate part. Saturated hydrocarbons, monolefins and diolefins are observed in the C_4 to C_8 regions. The aromatic MTA spectra are somewhat similar (Figure 21). In addition to carbon oxides which are the main products, small amounts of water, benzene, and phenol are observed. The 1,4-phenylene polymers also give quinone in small amounts. The relatively simple spectra for the aromatic polymers were analyzed to give the quantitative data shown in Table X. Comparison of Tables IX and X shows that the carbon monoxide/dioxide ratio is generally greater under MTA conditions than under isothermal MS conditions.

In addition to obtaining the above product information, it is useful to examine the overall ion intensity-temperature profiles. This gives further information regarding the main degradation and char-forming mechanisms. One feature which is immediately obvious is that in contrast to the previously studied aliphatic systems where all the products appeared simultaneously, the products from the semiaromatic and aromatic polymers are not all identical with respect to starting, peaking, and finishing temperatures.

TABLE X

MASS THERMAL ANALYSIS OF VOLATILES FROM AROMATIC POLYMERS

PRODUCT	PI 480°C*	PT (mole%) 575°C*	PP 550°C*	BP 500°C*	BP 575°C*
Carbon Monoxide	40	55	62	25	28
Carbon Dioxide	47	21	22	75	45
Water	6	8	5	–	6
Benzene	7	8	6	–	20
Quinone	–	8	4	–	–
Phenol	trace	< 1	trace	–	< 1
Benzaldehyde	trace	trace	trace	–	–
Benzoic Acid	–	trace	–	–	–
Toluene	–	–	–	–	trace

* Observed MTA peak temperature for most of the components of the major weight-loss step

In HT, most of the products appeared around 300°C but water started later at around 350°C. A most surprising feature of the spectra was the appearance of products at temperatures over 500°C. These were benzene, carbon monoxide, and carbon dioxide. Since TGA showed complete weight loss at 500°C it was surmised that these products derived from further degradation of the condensate fraction. PS exhibits a more complex degradation. Some succinic anhydride is evolved at very low temperatures (130°-250°C) indicating further condensation or destruction of succinic end structures. The major weight-loss step begins at 275° to 300° with evolution of the anhydride, carbon monoxide, and carbon dioxide. Water and butadiene appear at about 350°. These processes all persist to high temperatures and are accompanied above 400° by aromatic structures such as quinone, benzene, and phenol. A little hydrogen is also observed starting at about 450°C. For the corresponding sebacate polymer, SP, destruction of the ester grouping takes place first (300°) followed by fragmentation of the sebacate chain starting at around 350° and formation of aromatic products and water at around 400°. Since the TGA residue was very small in SP, the significance of the high temperature products is uncertain. This feature is disturbing since, if products appear when degradation should be complete, it is difficult to know which products are characteristic of the char-forming process in residue-forming degradations. In the latter, it is probable that products actually derive for both degradation of the residue and further degradation of condensate fraction.

The aromatic polymers generally show decarboxylation as the first degradation process with decarbonylation at significantly higher temperatures. PP, however, showed both processes simultaneously. Water and aromatic products were evolved in all cases but it is difficult to generalize as to the temperature difference for the formation of the various products relative to the carbon oxides. At higher temperatures ($>500°$) some hydrogen and methane were observed for PI and PP. Water formation was especially interesting in those polymers as it often took the form of a complex, broad band over the temperature range $400°$ to $1000°$. At high temperatures, a probable mechanism for water formation is the dehydration between phenolic end-groups and hydrogen atoms from adjacent rings.
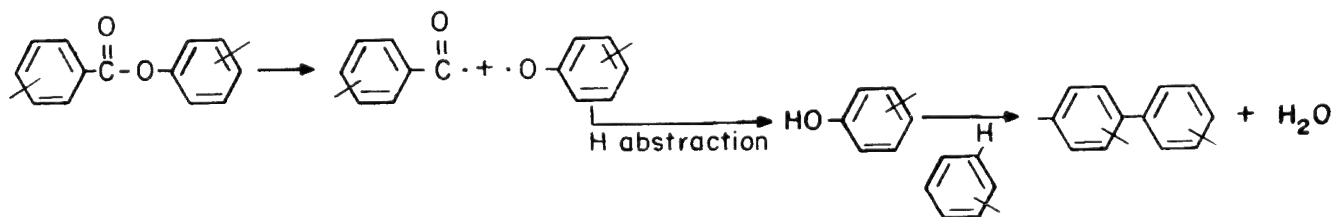
Sometimes, more than one peak was indicated. The major products CO and CO_2 usually fall after the main peak and maintain some evolution at higher temperatures. The carbon dioxide falls more than the carbon monoxide so that the CO/CO_2 ratio is higher at high temperatures than during the early stages of degradation. Both PI and PP appear to give a second CO peak at high temperatures. The temperature differential between CO and CO_2 production for PT and PI explains why the isothermal MS analysis gives a lower CO/CO_2 ratio than the dynamic MTA analysis (Tables IX and X).
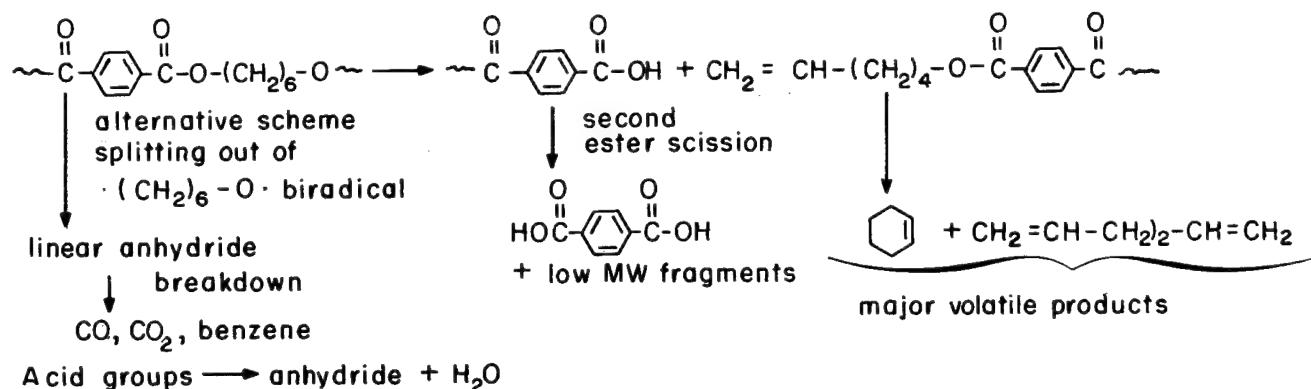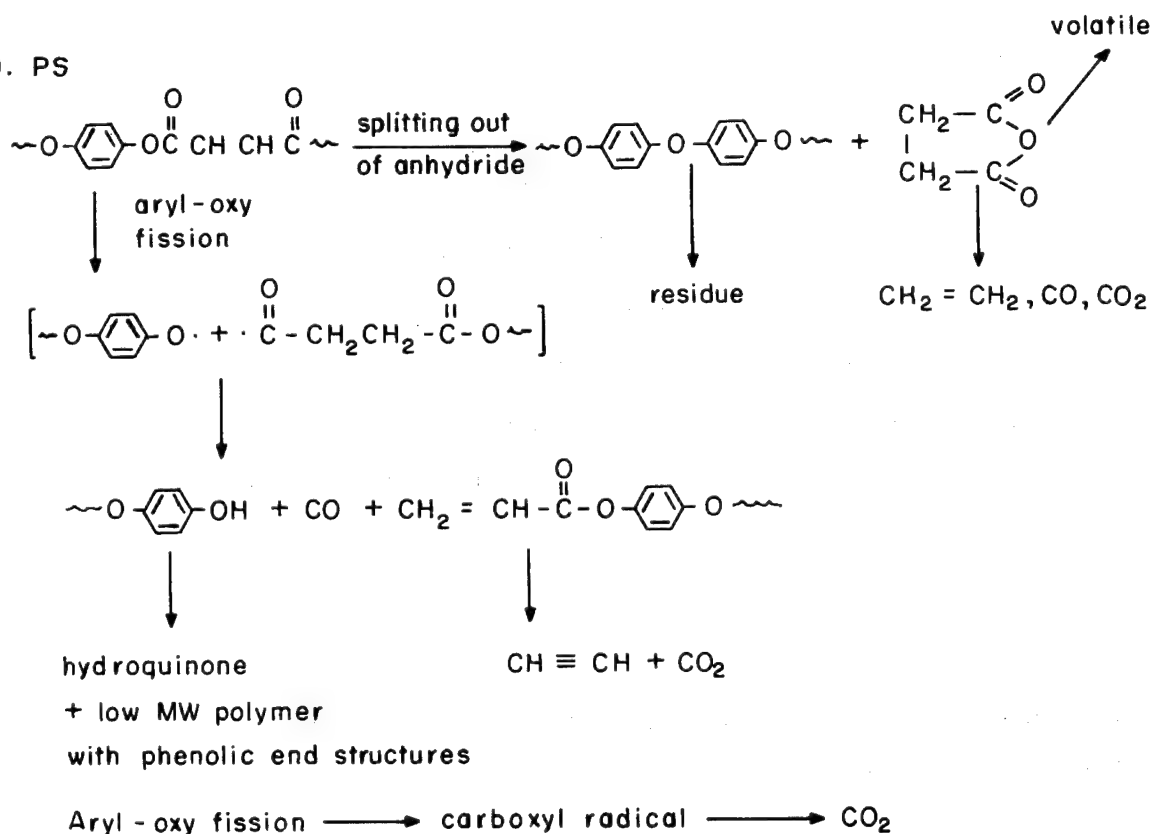
3. MECHANISMS

a. Semiaromatic Polymers

From the MTA evidence, volatile products derive from the aliphatic part of the polymer although it must be remembered that small aromatic species can be present in the condensate fraction. The most striking feature is the small amount of carbon oxides from HT compared with PS and SP. Aromatic carboxylic groups are clearly more stable to decarboxylation and decarbonylation than aliphatic ones. No concise mechanism can account for all the products.

(1). HT

alternative scheme
splitting out of
· (CH₂)₆ - O · biradical

second
ester scission

linear anhydride
breakdown

CO, CO_2, benzene

$HOC \bigcirc C\text{-}OH$
+ low MW fragments

$\bigcirc$ + $CH_2 = CH - CH_2)_2 - CH = CH_2$

major volatile products

Acid groups ⟶ anhydride + H_2O

(2). PS

volatile

splitting out
of anhydride

residue

$CH_2 = CH_2, CO, CO_2$

aryl-oxy
fission

$[\sim O \bigcirc O \cdot + \cdot \overset{O}{\overset{\|}{C}} - CH_2CH_2 - \overset{O}{\overset{\|}{C}} - O \sim]$

$\sim O \bigcirc OH + CO + CH_2 = CH - \overset{O}{\overset{\|}{C}} - O \bigcirc O \sim$

hydroquinone
+ low MW polymer
with phenolic end structures

$CH \equiv CH + CO_2$

Aryl-oxy fission ⟶ carboxyl radical ⟶ CO_2

(3). SP

Similar mechanism to PS except that concerted anhydride reaction cannot take place. The presence of phenolic and acid end structures suggests that both acyl-oxy and aryl-oxy scissions can occur. Owing to larger aliphatic chains in SP, cross-linking by radical intermediates gives a less tightly packed network then in PS. The loosely cross-linked structure breaks down further as the temperature is raised to give a small residue whereas the more tightly cross-linked structure in PS does not decompose appreciably and forms a highly carbonized char.
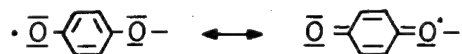
b. Aromatic Polymers

Degradation starts with scission of the ester group:
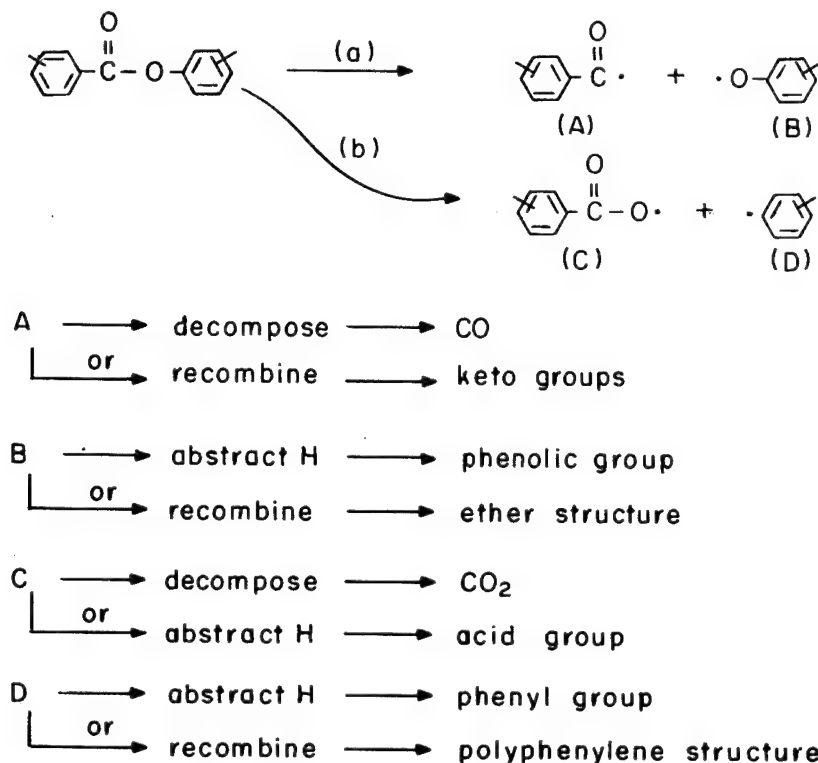
NOTES:

(1) H abstraction gives further radicals which can combine to give cross-linked structure which forms residue and char.

(2) Adjacent ester scissions give low MW products (condensate) with a variety of end-structures.

(3) The probability of (a) and (b) depends both on temperature and the aromatic structures involved. In both PT and PI reactions (b) is most probable initially with reaction (a) becoming more prominent as the temperature is increased. The resonance stabilization of radical (B) is probably an important factor. In the p-phenylene polymers such a radical is stabilized thusly:

PT and PP therefore favor reaction (a) and give more carbon monoxide than dioxide. PI, however, cannot have this stabilization in the m-phenylene moiety and undergoes reaction (b) to the greater extent so that CO_2 production outweighs CO production.

SECTION V
CONCLUSIONS

The foregoing study of semiaromatic and aromatic polyesters indicates that degradation takes place by random scission of the ester links. Carbon dioxide is generally the first gaseous product to be evolved. With the exception of polymer HT, the degradation becomes extremely complex and this is reflected both in the kinetics of degradation and the product temperature profiles obtained by MTA.

Poly(hexamethylene terephthalate) degrades in a similar fashion to the aliphatic polymers previously studied. Random scission gives low MW ester fragments and the considerable amount of olefinic product probably derives from secondary breakdown of olefinic chain ends produced by ester scission. The arylene succinate and sebacate polymers degraded in a more complex manner. Although the type of scission previously postulated for aliphatic polyesters was not appreciable, the polymers showed no increase in thermal stability. In fact, the semiaromatic polymers appeared to be less stable than the aliphatic systems. Cross-linking takes place in the arylene polymers; in SP, the cross-linked polymer breaks down at higher temperatures giving a second maximum to the DTG curve, but for PS a residue is formed which loses weight very slowly up to about 1000°C. The MTA analyses showed that the various products did not all appear at the same temperature and that degradation consists of a mixture of overlapping reactions. This fact would tend to invalidate the kinetic analysis and perhaps explains the difficulty of obtaining constant E_a-conversion trends. It must be remembered, however, that most of the weight loss consists of the condensate fraction and products directly corrected with the ester scission, namely CO and CO_2. The obtained kinetic parameters may still be considered as being significant. It is interesting that although the measured activation

energies of HT and PS were higher than those of the aliphatic polymers, the semiaromatic polymers appeared less stable with respect to initial rates of degradation. This may be a result of end-groups which are probably more susceptible to decarboxylation and other reactions in the aromatic compounds than in aliphatic ones. End-capping the polymers may have eliminated this apparent instability.

Much of the above discussion on semiaromatic polymers applies to the fully-aromatic polyesters. The gaseous products appear at different temperatures with carbon dioxide usually the first product. At high temperatures, carbon monoxide, water, and small aromatic products appear, and at very high temperatures, hydrogen, acetylene, and methane may appear. As expected, the thermal stabilities of the aromatic systems are higher than the aliphatic and semiaromatic polymers; the thermal stability was greatest for esters containing the 1, 4 phenylene moiety. Both acyl-oxy and aryl-oxy scission take place under dynamic conditions initially by a random process. The evolution of products such as low MW fragments and small aromatic species must involve hydrogen abstraction from adjacent benzene rings. This produces cross-linking and residue formation above $500^{\circ}C$. The evolution of condensate fraction ceases (Reference 8) as would be expected from extensively cross-linked material. Gaseous products persist from decomposition of remaining ester groups, cross-linking, dehydrogenation, and further fragmentation.

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9(b) Ibid, p. 125.

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13. H. L. Friedman, ML-TDR-64-274, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, Part I (August 1964); Part II (October 1965).

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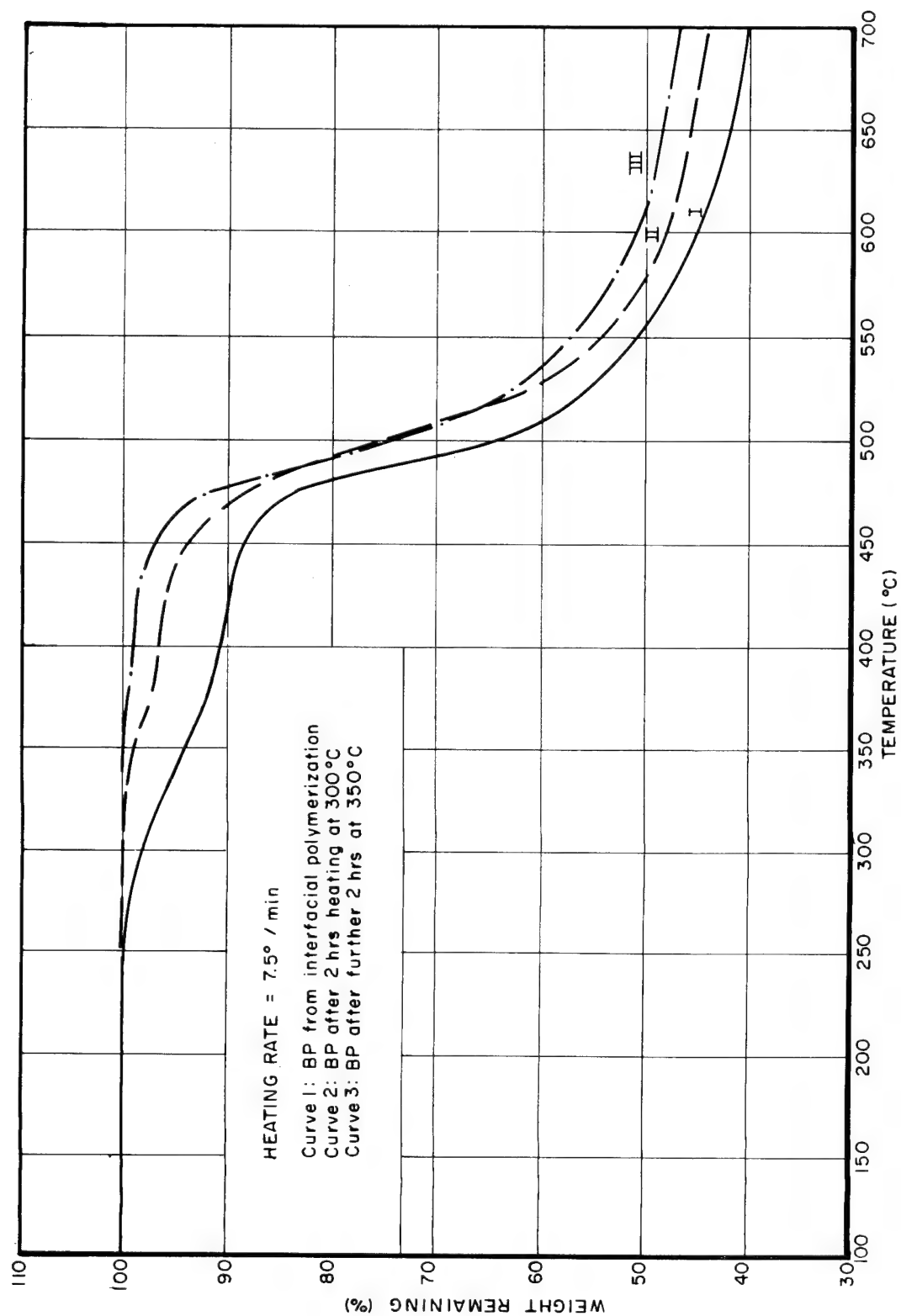15. J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, $\underline{A70}$(6), 487 (1966).

Figure 1.   Effect of Heat Treatment on TGA of Polymer BP

HEATING RATE = 7.5° / min

Curve 1: BP from interfacial polymerization
Curve 2: BP after 2 hrs heating at 300°C
Curve 3: BP after further 2 hrs at 350°C

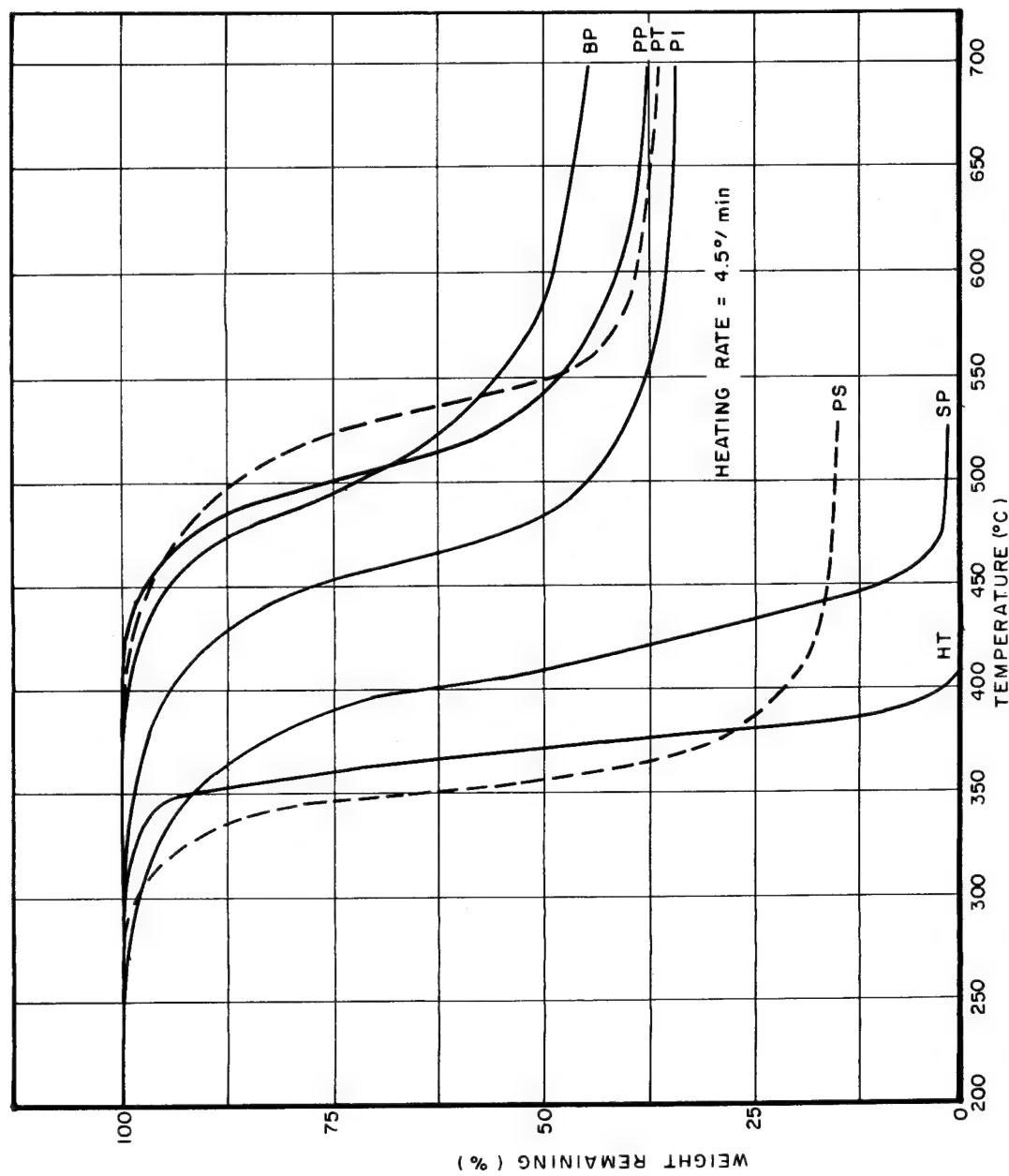TEMPERATURE (°C)

WEIGHT REMAINING (%)
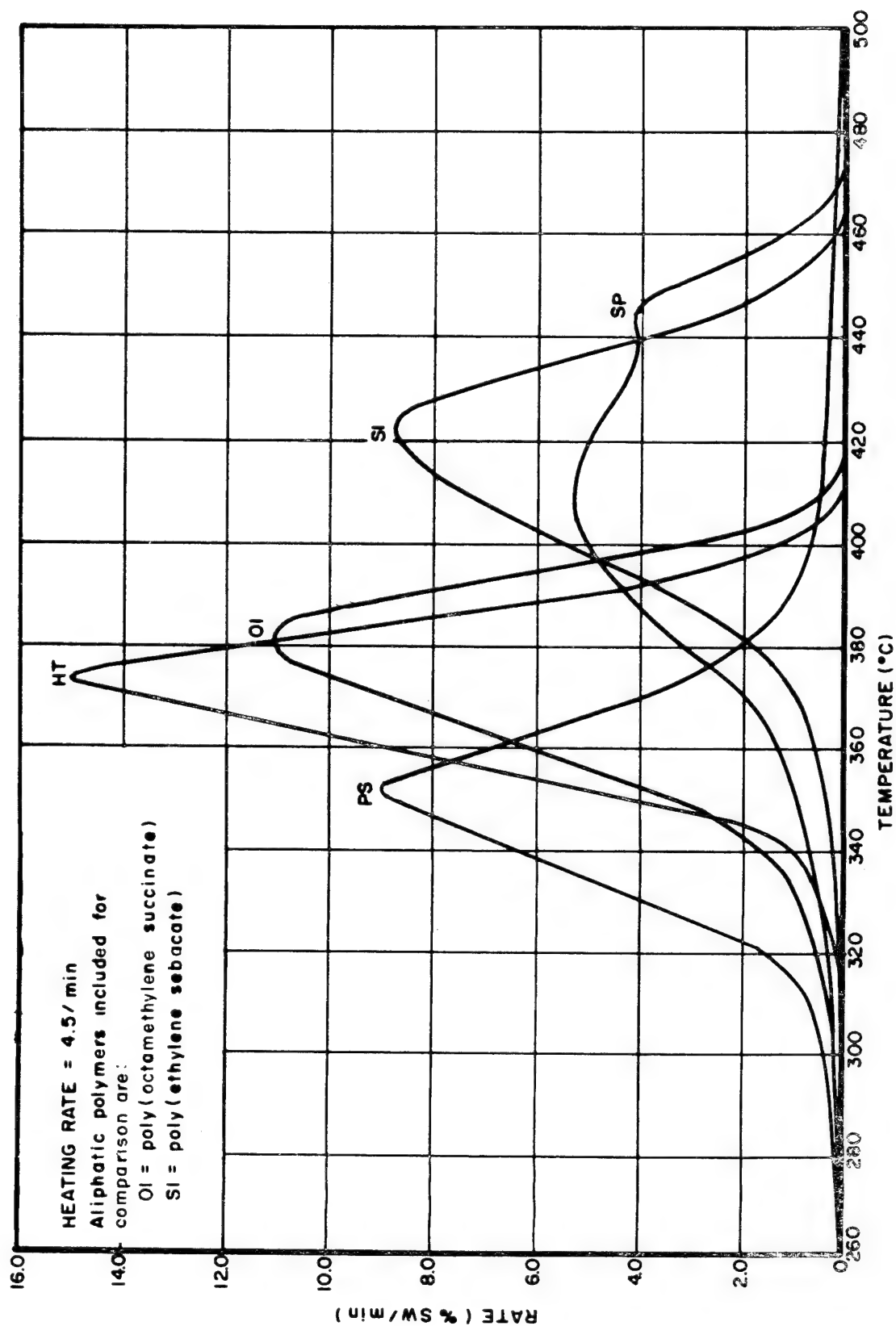
26

Figure 2. Representative TGA Curves
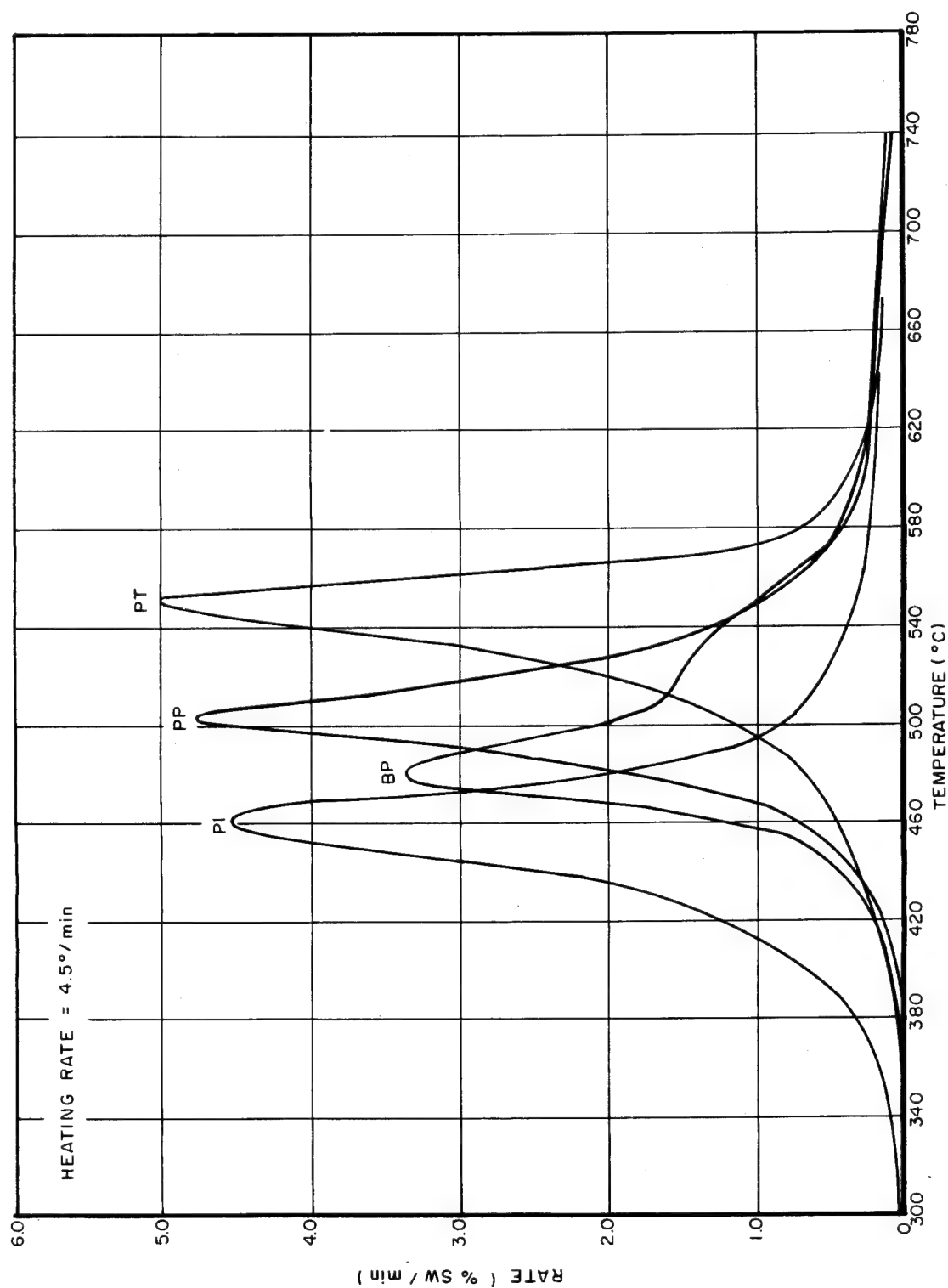
27

Figure 3.   DTG Curves of Semiaromatic Polyesters
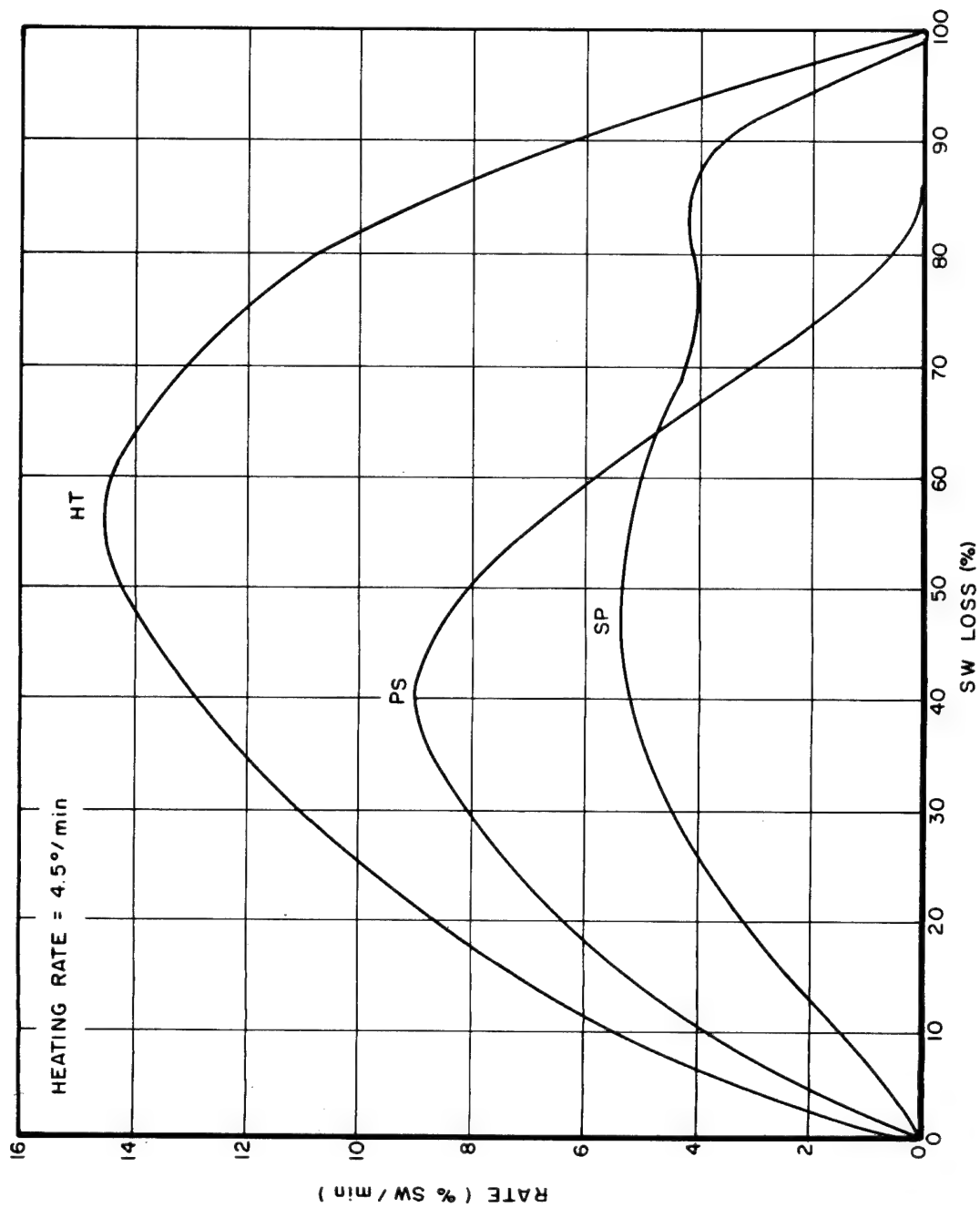
28

Figure 4.   DTG Curves for Aromatic Polyesters
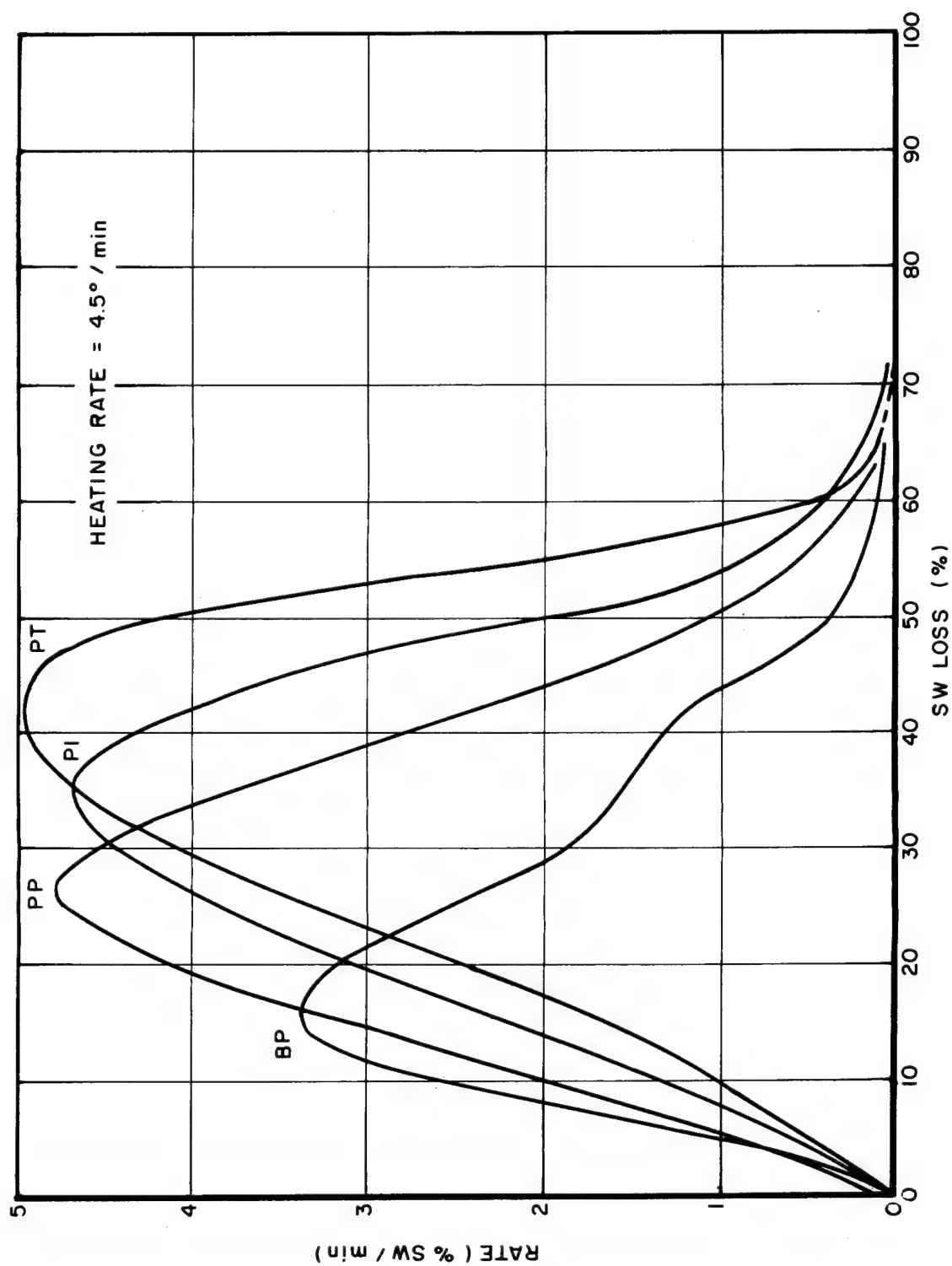
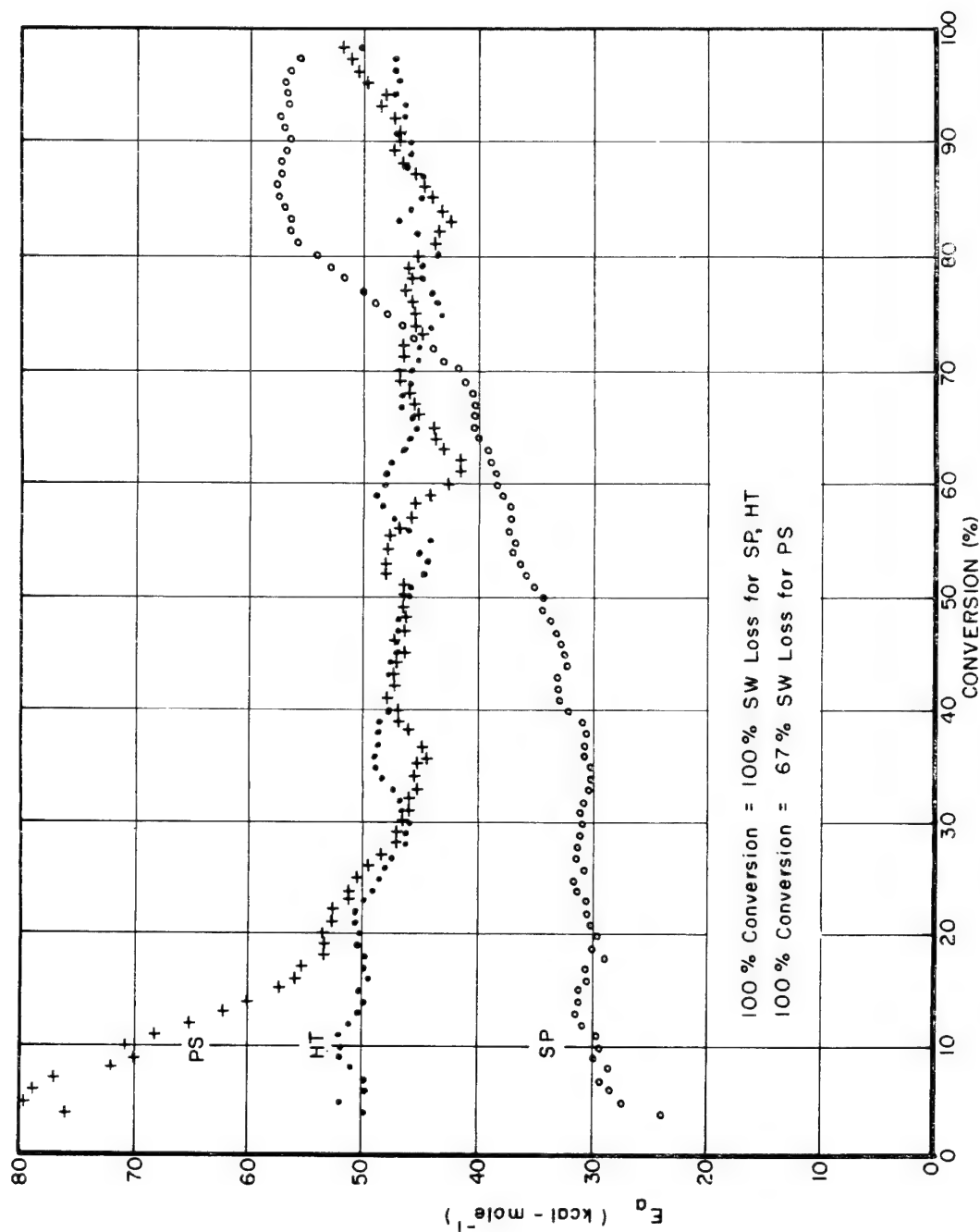Figure 5. Rate-Conversion Curves for Semiaromatic Polymers

Figure 6.   Rate-Conversion Curves for Aromatic Polymers

100 % Conversion = 100 % SW Loss for SP, HT
100 % Conversion = 67 % SW Loss for PS

Figure 7. Activation Energy-Conversion Relationships for Semiaromatic Polyesters

AFML-TR-68-182
Part II
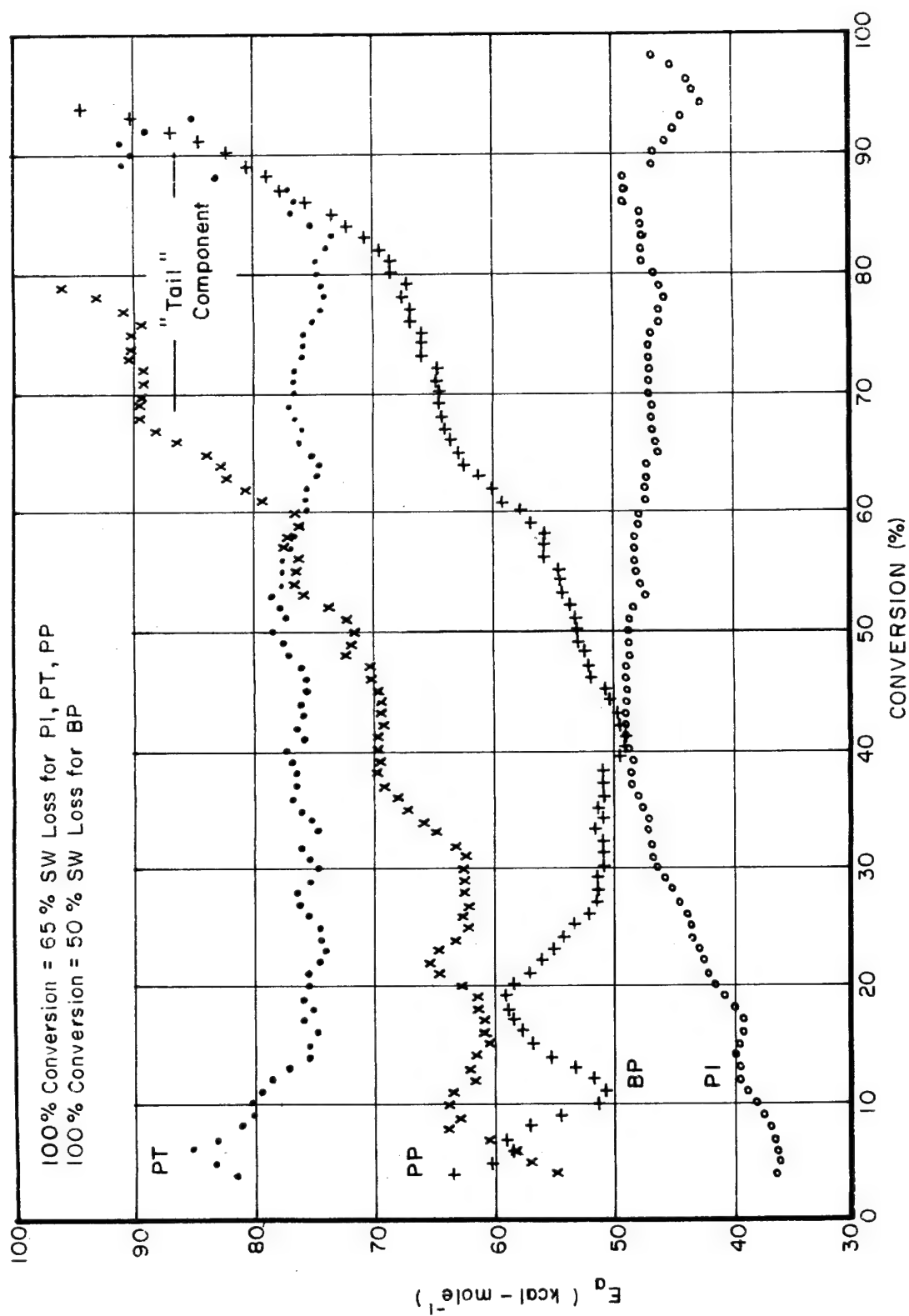
Figure 8.   Activation Energy-Conversion Relationships for Aromatic Polyesters
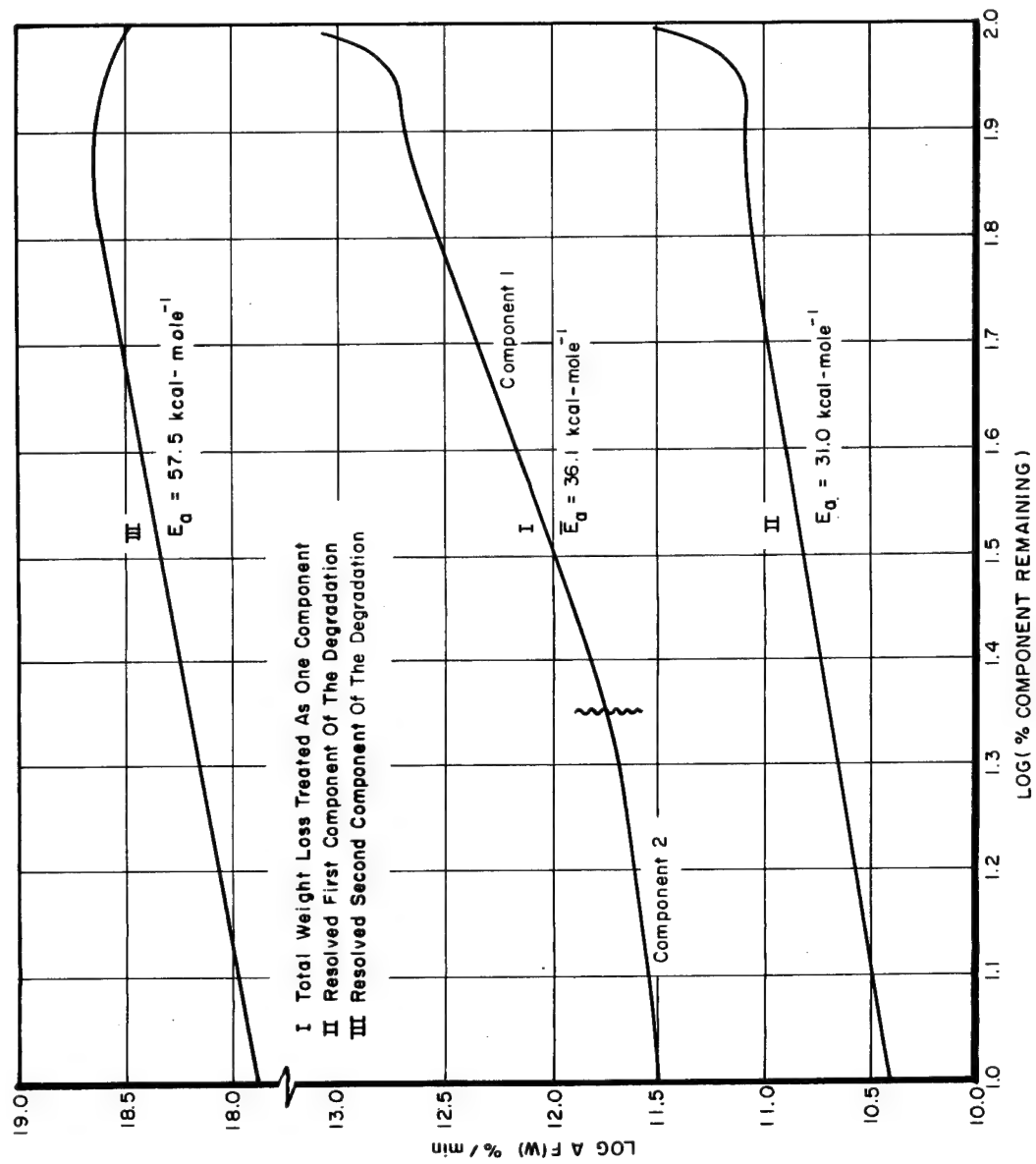
33
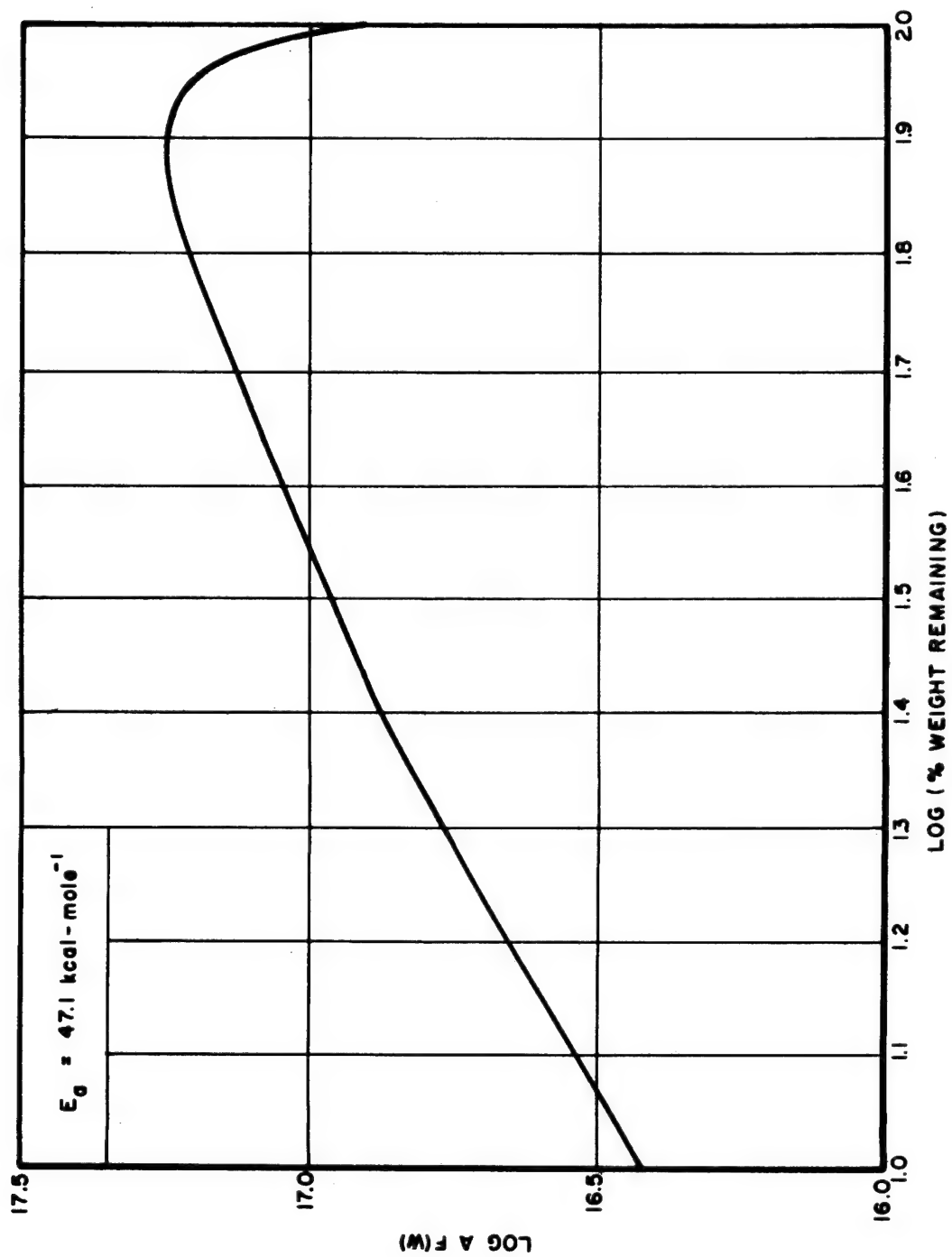
Figure 9.   Log A F(W) Curve for Polymer HT

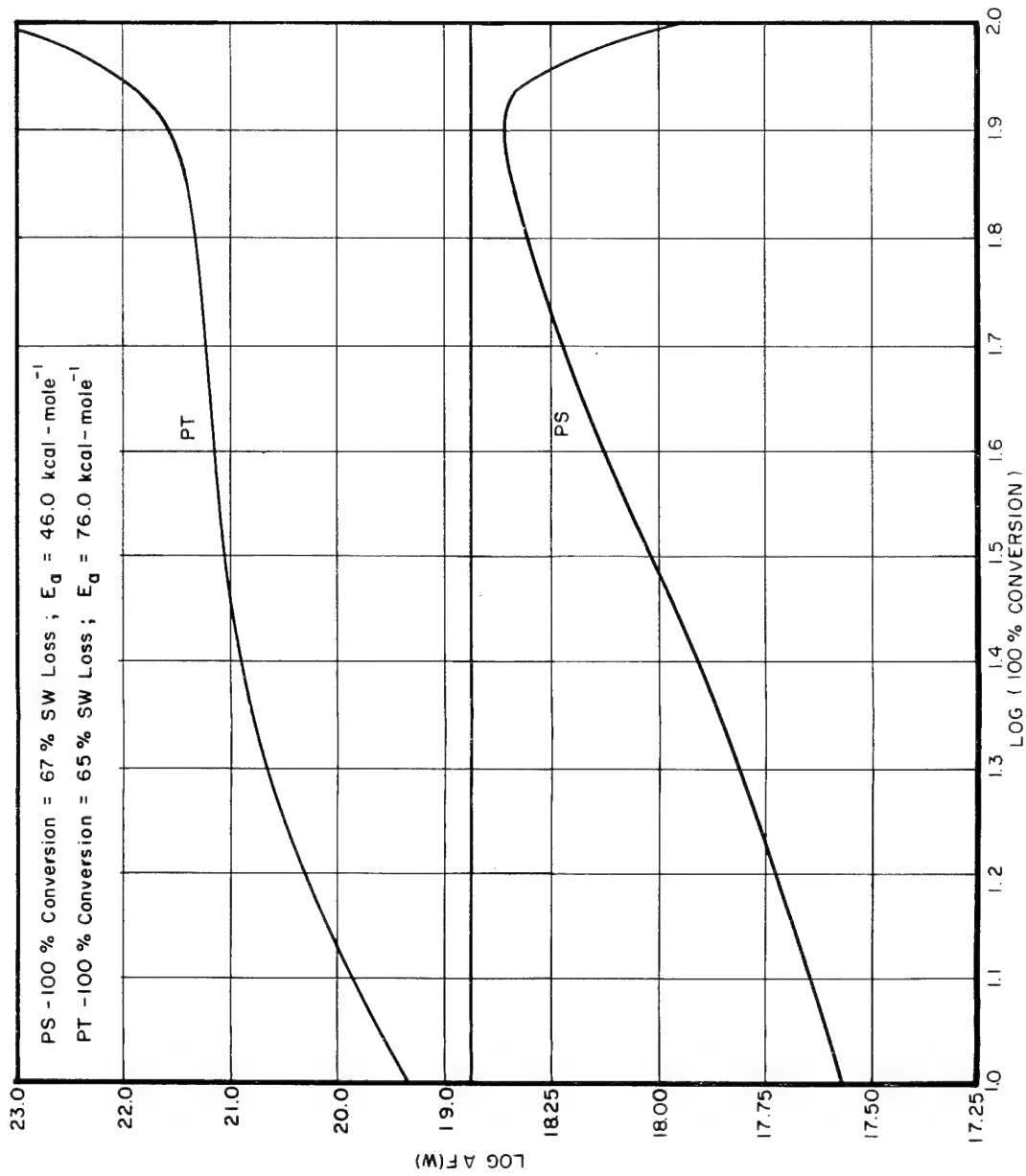Figure 10. Log A F(W) Curves for Polymer SP

PS - 100 % Conversion = 67 % SW Loss ; E_a = 46.0 kcal - mole^{-1}

PT - 100 % Conversion = 65 % SW Loss ; E_a = 76.0 kcal - mole^{-1}

PT

PS

LOG A F(W)

23.0

22.0

21.0

20.0

19.0

18.25

18.00

17.75

17.50

17.25

1.0   1.1   1.2   1.3   1.4   1.5   1.6   1.7   1.8   1.9   2.0

LOG (100 % CONVERSION)

Figure 11.   Log A F(W) Curves for Polymers PS and PT

PI: E_a = 48.1 kcal-mole^{-1}, 100 % Conversion = 65 % SW Loss
BP: E_a = 56.4
PP: E_a = 62.0 } 100 % Conversion = 50 % SW Loss
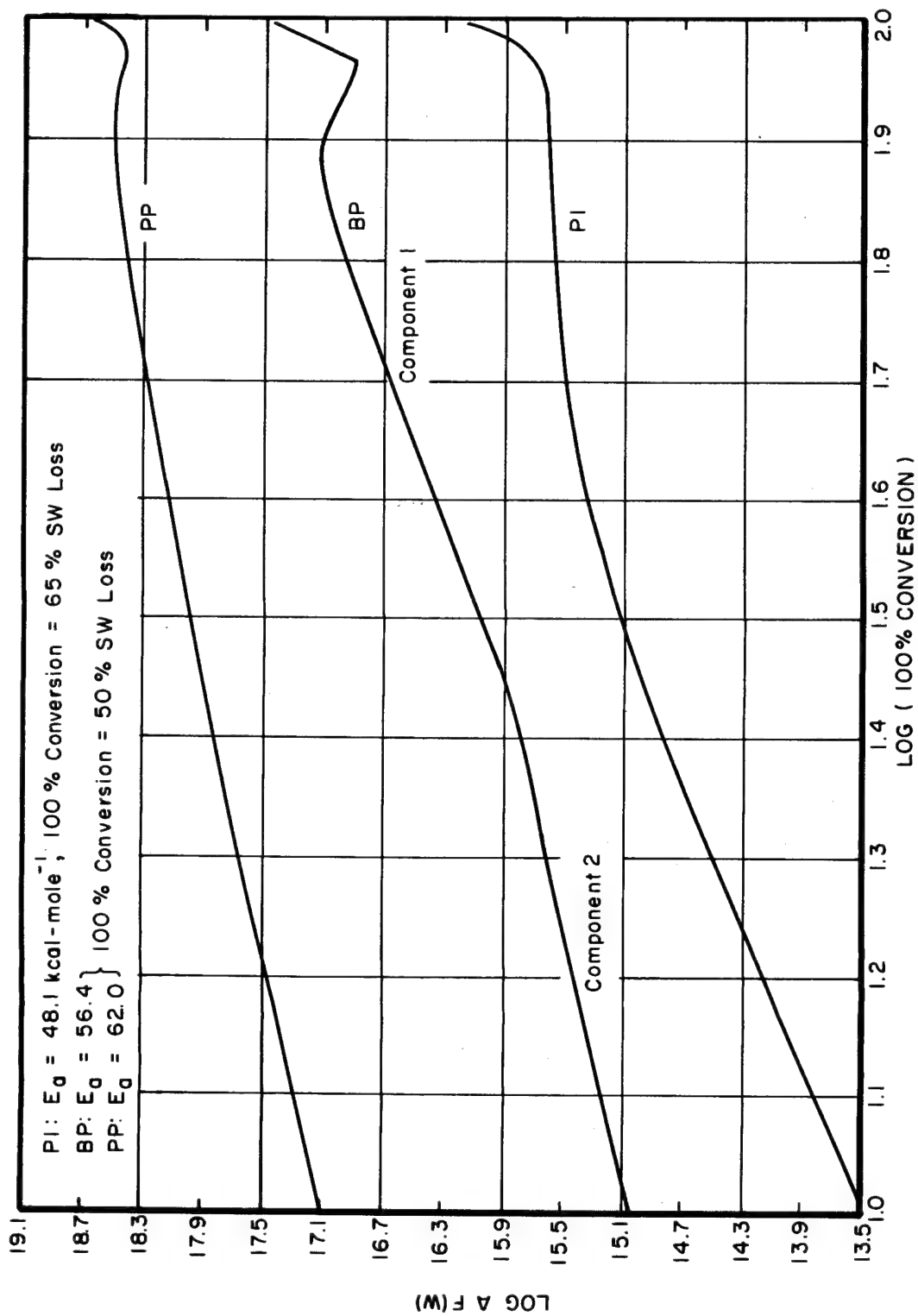
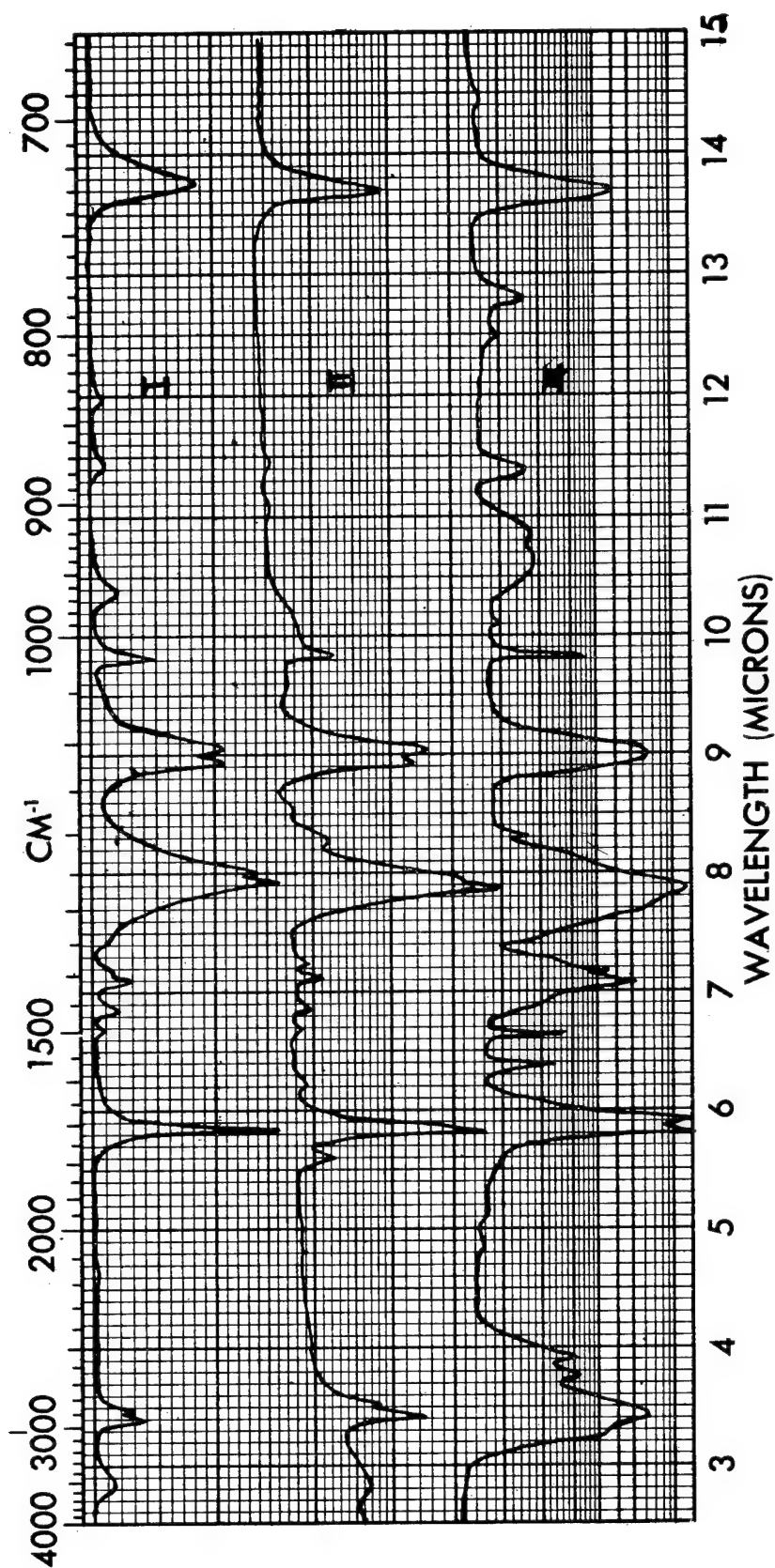Figure 12.   Log A F(W) Curves for Polymers PI, BP, and PP

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Figure 13.   IR Spectra of I: Polymer HT; II: Residue from Partial Degradation;
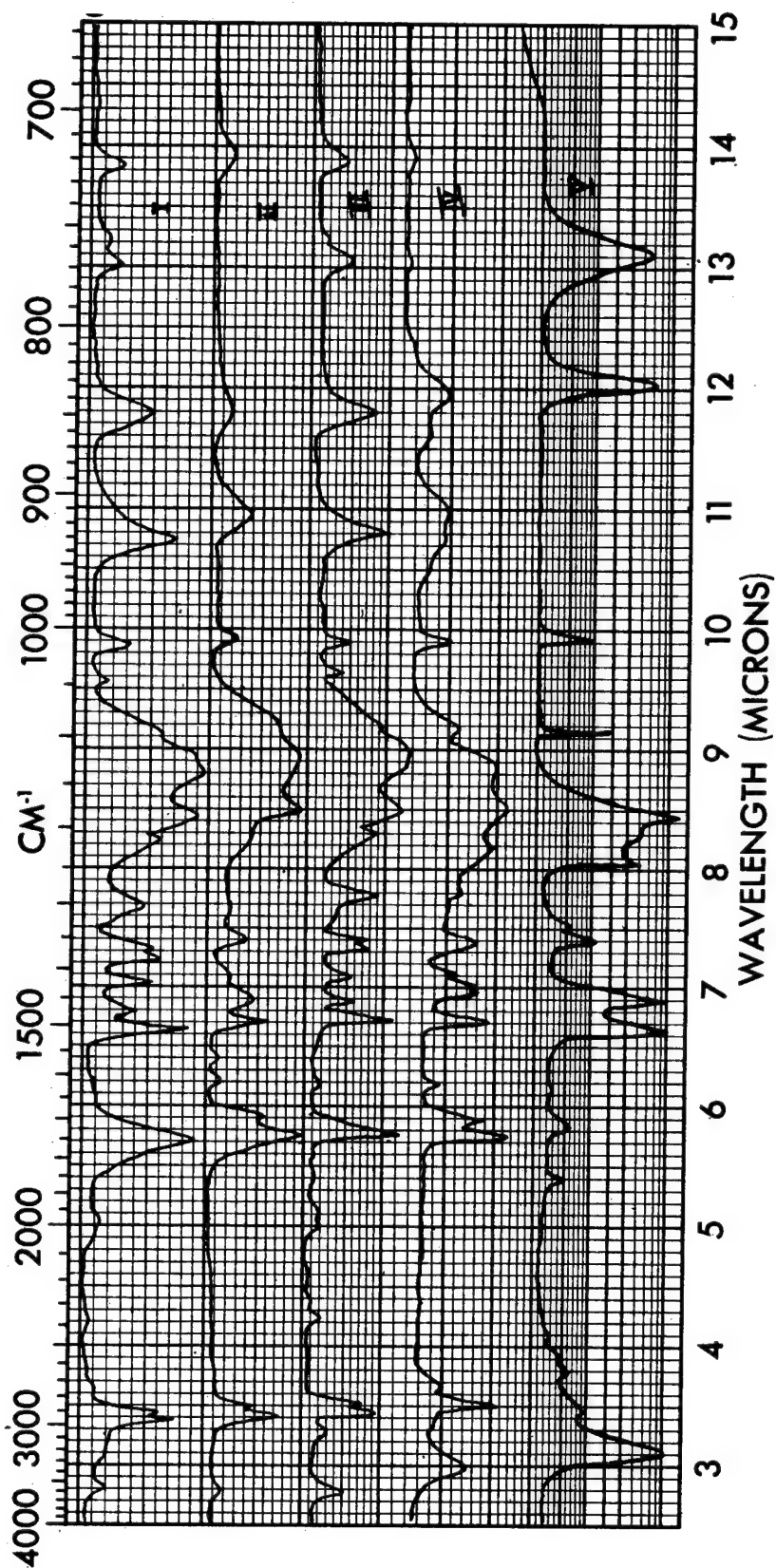III: Condensate

Figure 14. IR Spectra of I: Polymer SP; II: Residue from Partial Degradation; III: Bottom Condensate (nearest furnace); IV: Middle Condensate; V: Top Condensate
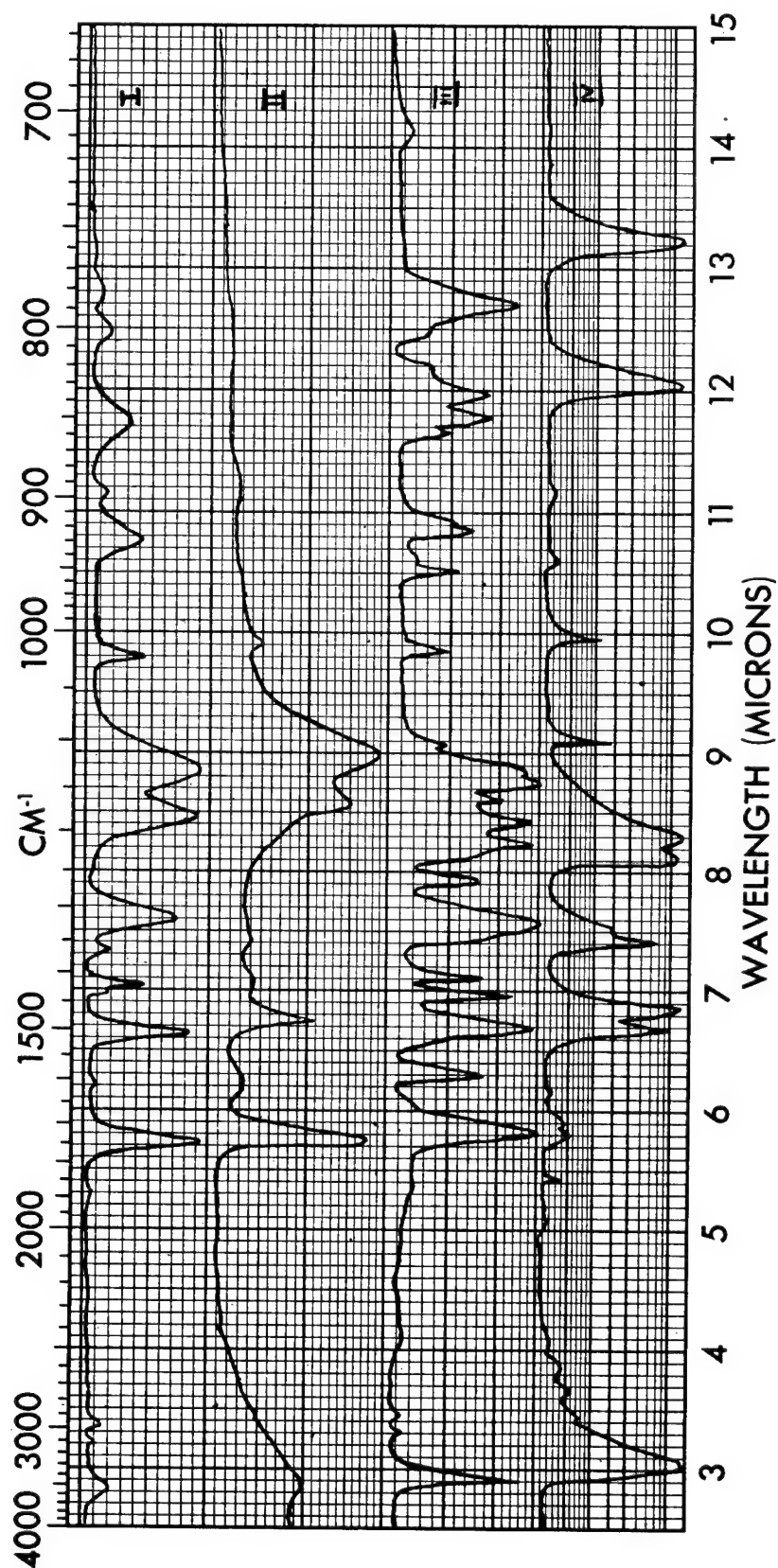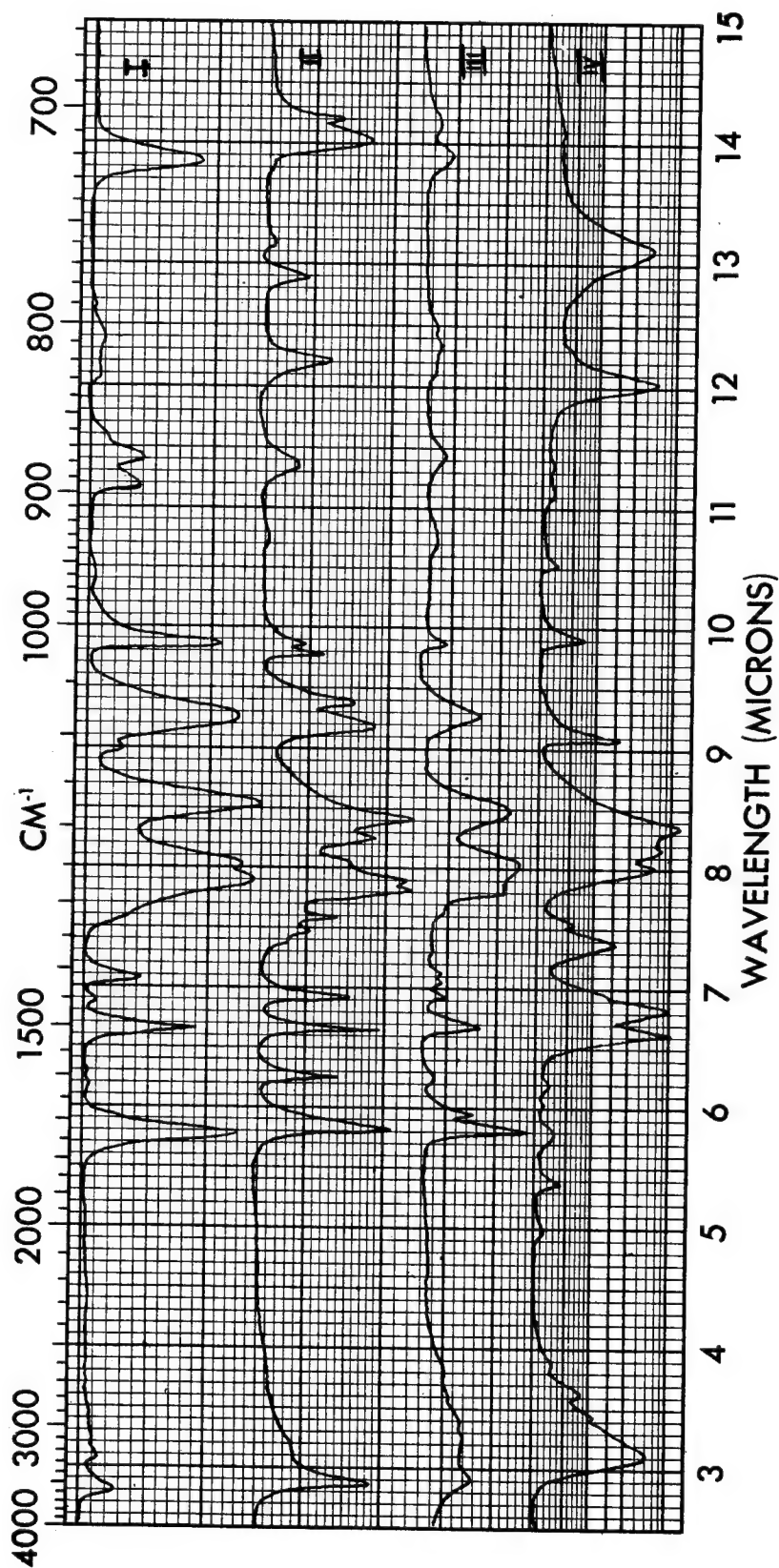
Figure 15.   IR Spectra of I: Polymer PS; II: Residue from Partial Degradation;
III: Lower Condensate; IV: Upper Condensate

Residue and bottom condensates are identical to I except for small band at 1660 cm^{-1} in the residue spectrum.

Figure 16.   IR Spectra of I: Polymer PT; II: Top Condensates; III: Middle
                    Condensates; IV: Scattered Crystals Above Condensates
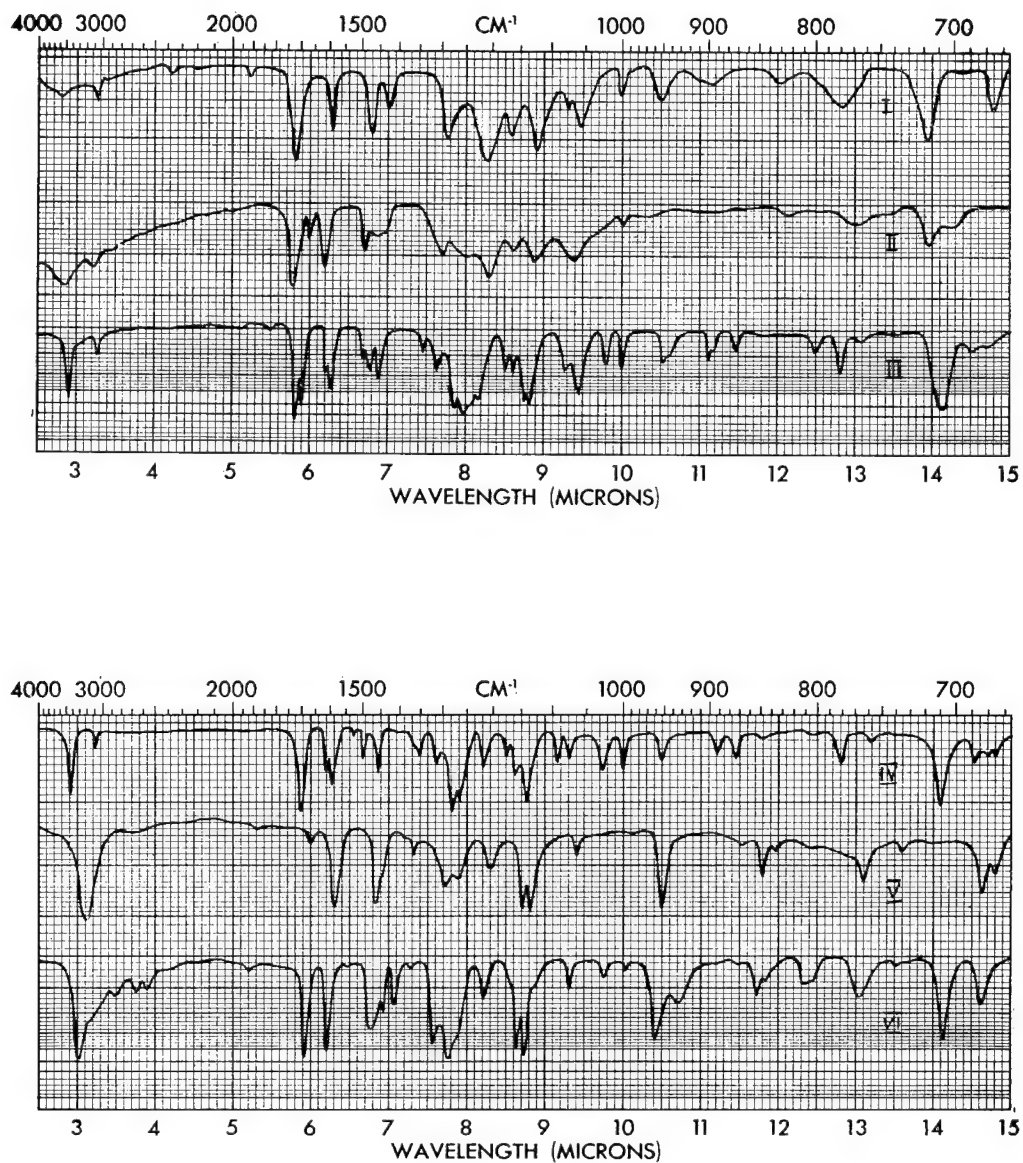
41

Figure 17.   IR Spectra of I: Polymer PI; II: Residue from Partial Degradation;
III: Bottom Condensate; IV and V: Middle Condensates; VI: Top
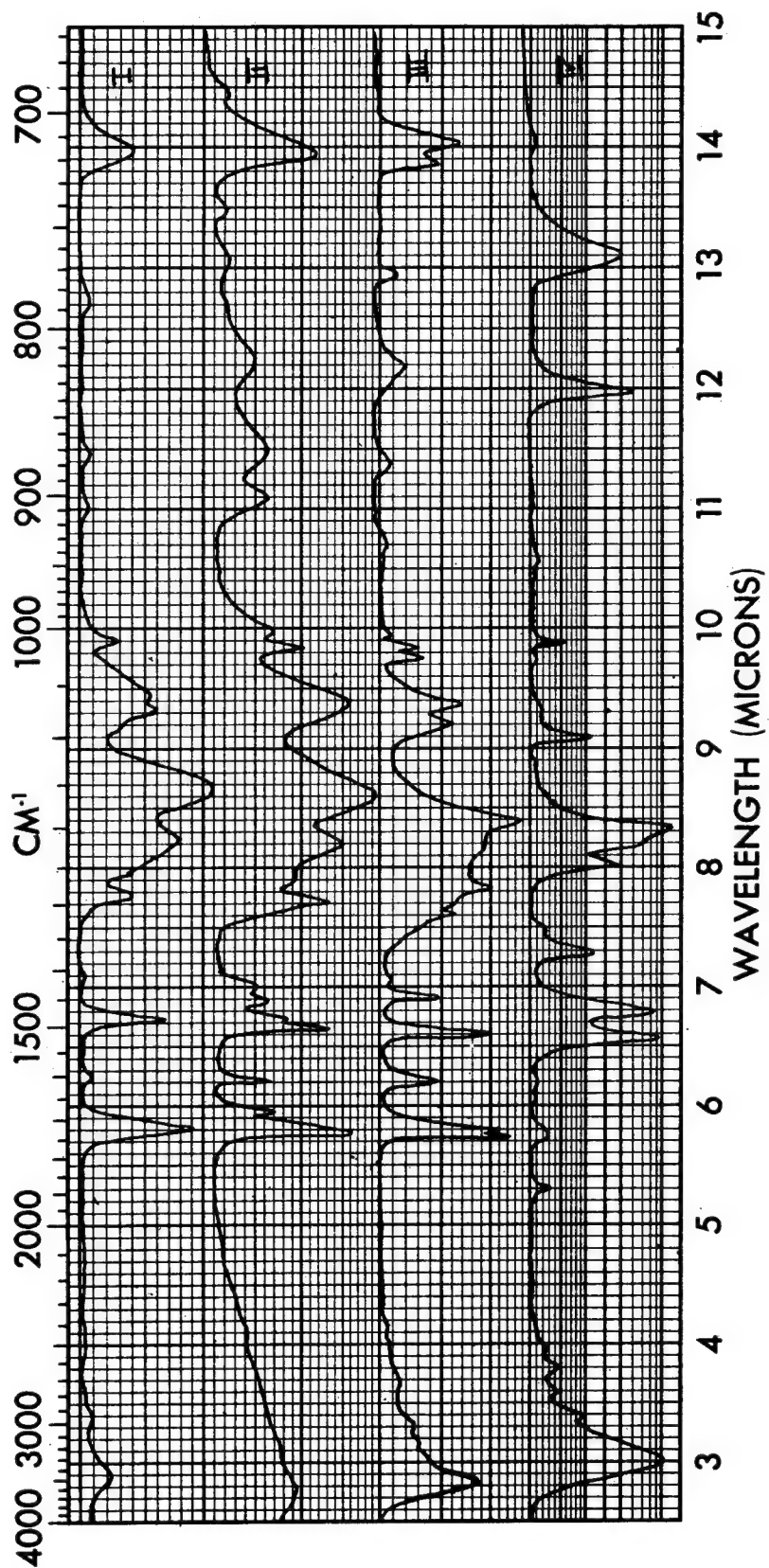Condensate

Figure 18.   IR Spectra of I: Polymer PP; II: Residue from Partial Degradation;
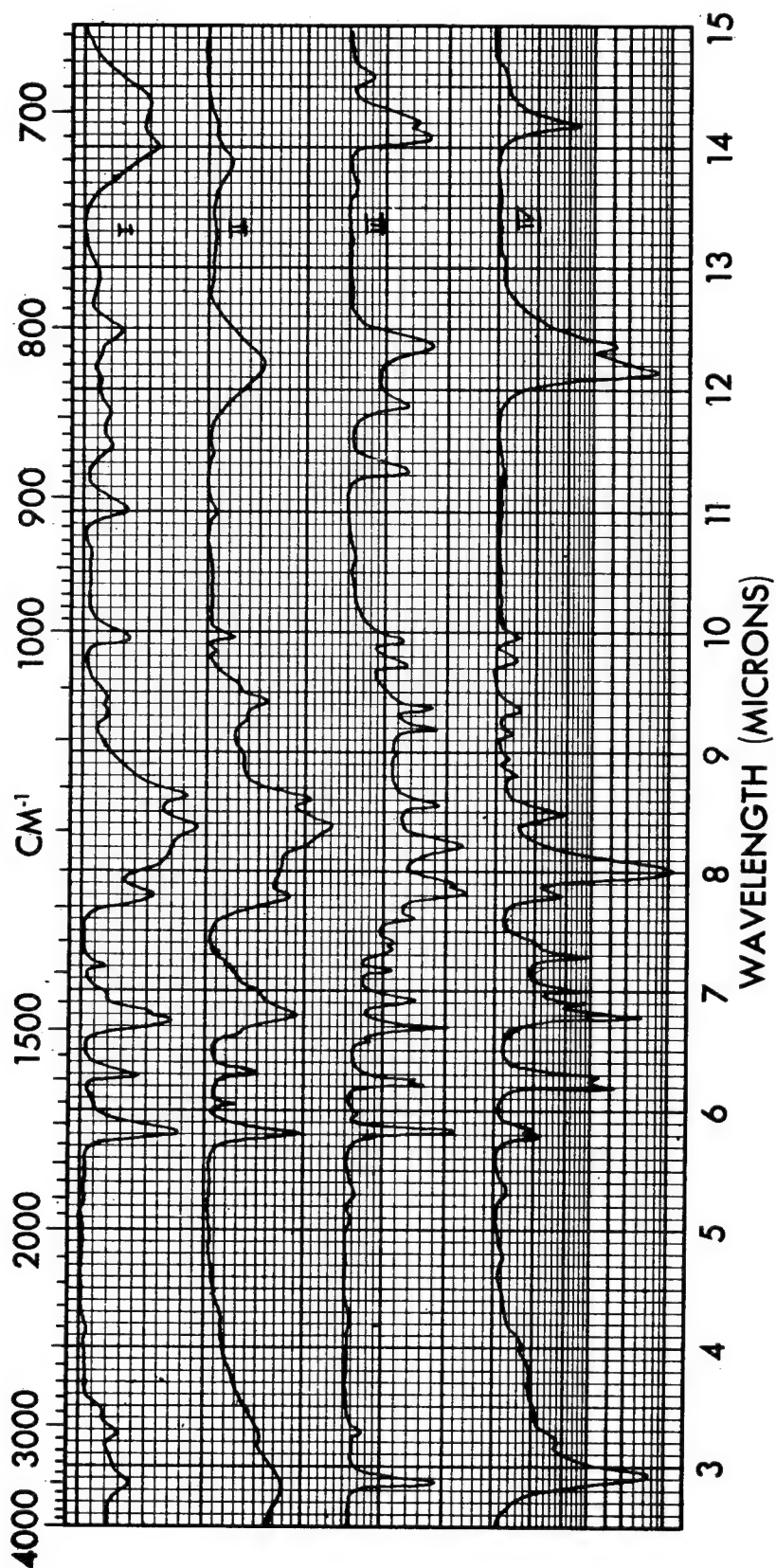III: Lower Condensate; IV: Upper Condensate

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Figure 19.   IR Spectra of I: Polymer BP; II: Residue from Partial Degradation;
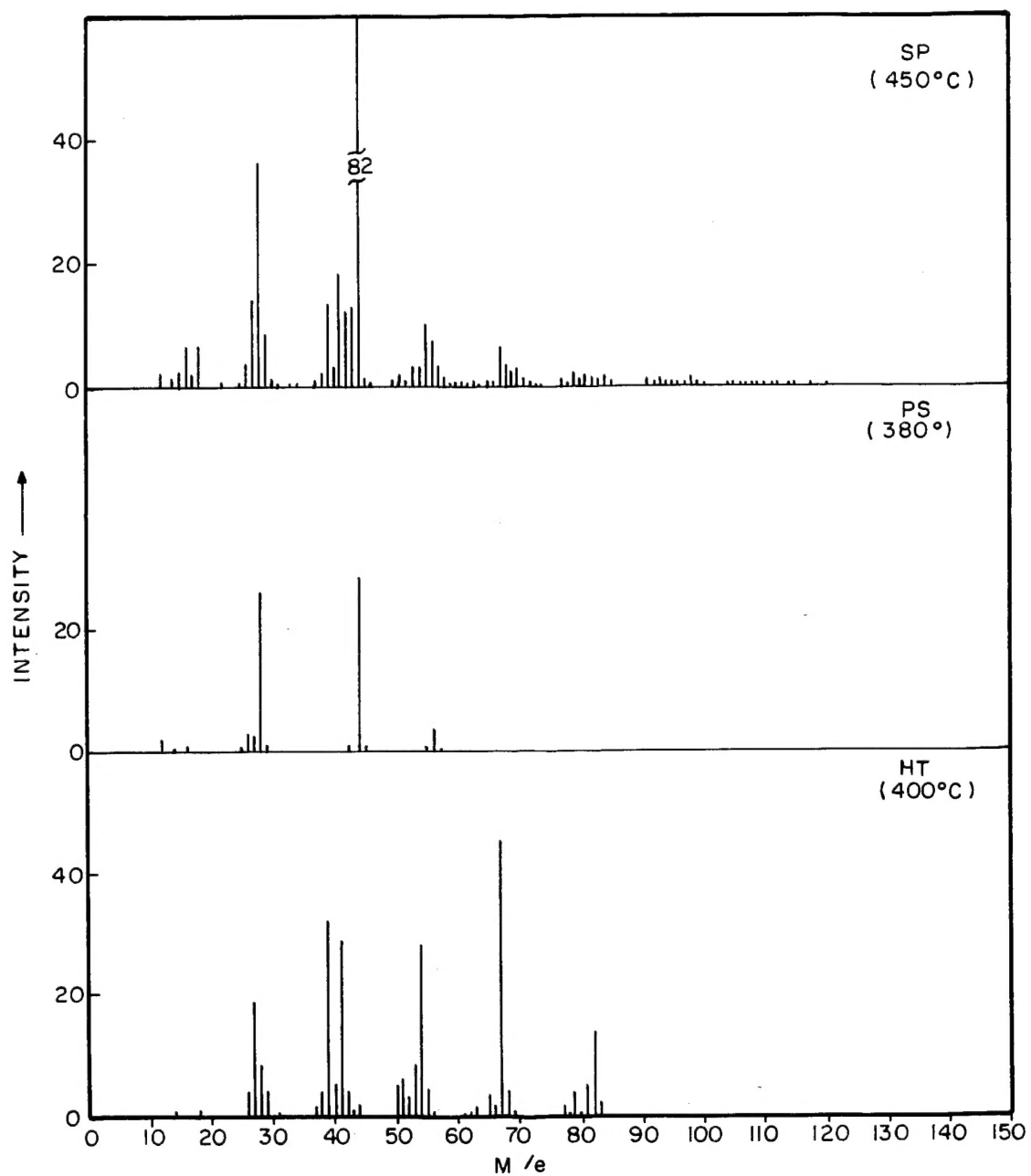III: Lower Condensate; IV: Upper Condensate

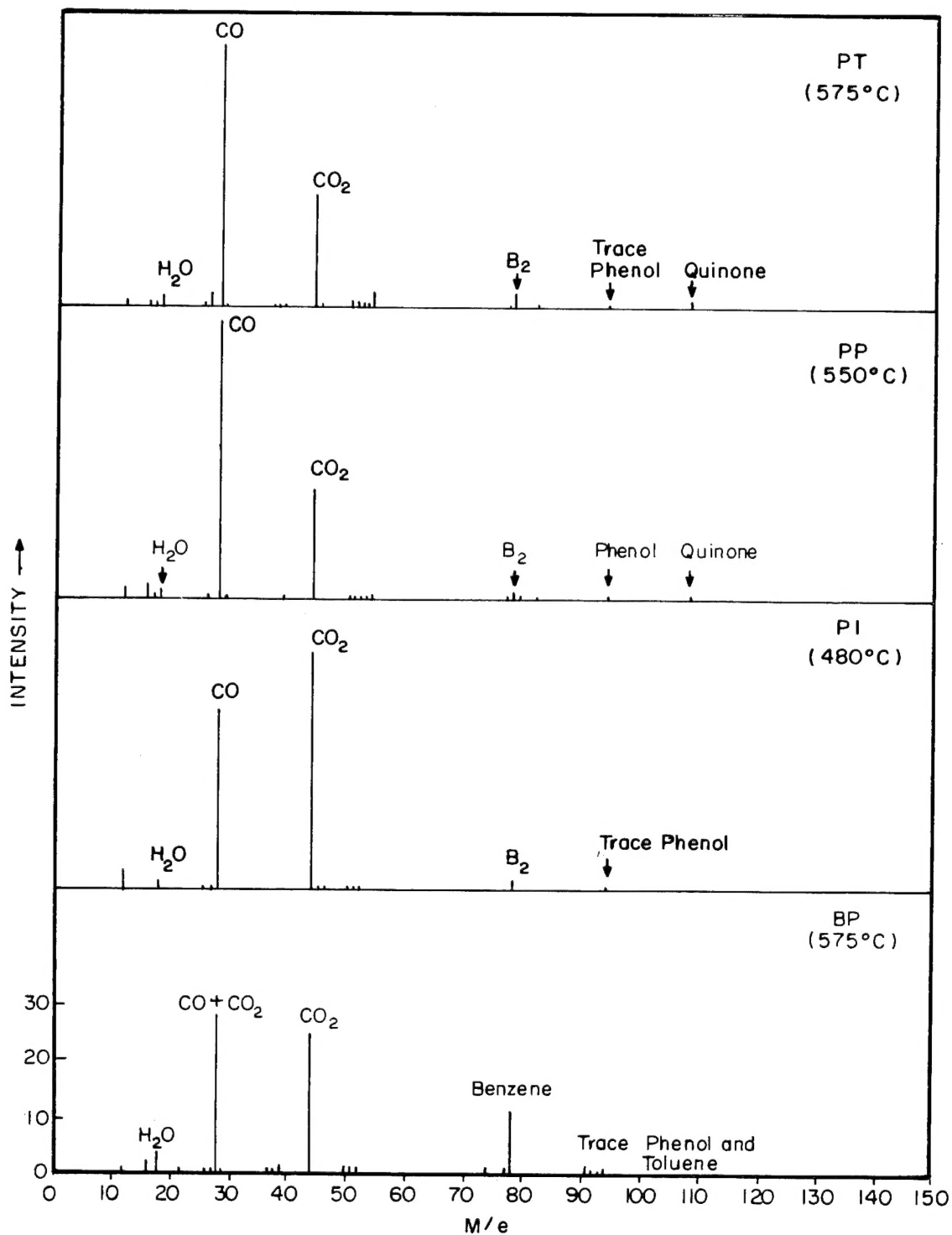Figure 20.   Mass Spectra From MTA Data for Semiaromatic Polymers

Figure 21.　Mass Spectra From MTA Data for Aromatic Polyesters

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13. ABSTRACT

A detailed study was made of the thermal degradation of eight aliphatic polyesters and the results presented in Part I of this report. The results of a corresponding study of some polyesters containing aromatic rings in the polymer chain are now presented in Part II.

Poly(hexamethylene terephthalate) degrades by the mechanism observed for aliphatic polymers -- random scission and subsequent reaction of the olefinic and acid end-groups. When the acid part is aliphatic as in poly(1,4-phenylene succinate) and poly(1,4-phenylene sebacate), the polymers are less stable initially than comparable aliphatic polyesters. The degradation mechanism is more complex and involves cross-linking; the cross-linked sebacate product breaks down by a second degradation reaction but the succinate forms a residue which does not undergo further breakdown.

Fully aromatic systems studied, namely poly(1,4-phenylene terephthalate), poly(1,3-phenylene isophthalate), poly(1,4-phenylene isophthalate-co-terephthalate) and poly(4,4'-biphenylene isophthalate), were more thermally stable, especially the all para system, and 35 to 45% of the initial weight remained at $800^{\circ}C$. Features such as initial low activation energy processes, complex rate curves with several components and char formation at high temperatures imposed difficulties in kinetic analysis of the degradations by programmed thermogravimetry.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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